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MINERAL AND METAL ZONING AND A RE-INTERPRETATION OF ISOTOPIC ZONING AT THE DARWIN Pb-Zn-Ag SKARN DEPOSIT, CALIFORNIA

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ABSTRACT

The +1 million ton Darwin Pb-Zn-Ag-W *skarn deposit* has been previously described as a group of sulfide replacement bodies zoned away from the mesothermal Darwin quartz monzonite pluton, and formed from magmatic fluids at $\simeq 350^{\circ}$C. Detailed surface mapping, however, indicates that the Pb-Zn skarn-sulfide bodies are appreciably (>20 Ma) younger than the Darwin pluton, and underground mapping/core logging indicates several *skarn*-sulfide "pipes" with strong concentric zoning. One of the pipes is zoned around a deep granite porphyry plug. The pipes exhibit outward zoning in wt% Pb/Zn and oz/ton Ag/wt%Pb (both

Combined mineral composition/assemblage and sulfur isotope systematics indicate that as the ore fluids flowed outward they experienced progressive decrease in oxidation state (~1 log unit) and increase in pH (1-2 units); upward moving fluids experienced initial decrease in oxidation state and increse in pH followed by a reversal to higher oxidation state and lower pH. The process of ore deposition was chemically complex and probably involved significant remobilization. Realistic ore depositinal models at Darwin require simultaneous changes in (at least) temperature, pH, and oxidation state, all of which were important.

INTRODUCTION

The Darwin district, in SE California (Fig. 1), contains Pb-Zn-Ag as well as Cu- and W-rich veins and skarns (Hall and MacKevett, 1962; Newberry, 1987). Production from the district includes more than 1 million tons of Ag-Pb-Zn ore, much of which was "direct shipping" high grade material, and 0.1 million tons of W ore. Average grades of sulfide ore mined after 1945 were approximatley 6% Pb, 6% Zn, 0.2% Cu and 6 oz/ton Ag (Hall and MacKevett, 1962). The Darwin deposit *per se* consists of a series of isolated Pb-Zn-Ag±W orebodies (Defiance, Thompson, Essex, Independence--Fig. 2) which were linked by a common haulage level in 1945.

Although a relatively small deposit, Darwin is notable for a pioneering S-isotope study (Rye et al., 1974) in which the authors integrated several light stable isotopes with the known geology; and for compative attempts at determining mineral formation temperatures ratios <.5 core, >1 margin). The pipes show mineralogical zoning, with a core defined by high sphalerite/galena, higher chalcopyrite, darker sphalerite, abundant pyrite inclusions in sphalerite, and evidence for multiple sulfide depositional events. Both graphite in marble and pyrrhotite in sulfide ores are zoned around the Darwin *pluton*, suggesting that pyrrhotite stability is influenced by pre-Pb-Zn skarn bleaching of marble beds. Garnets are highly complex, with 4 generations identified by petrographic and compositional relations; younger garnet typs are more abundant in upper and lateral parts of the pipe. Retrograde alteration of garnet is concentrated in the upper and laterally distal parts of the skarn, but garnet in apparent equilibrium with sulfide is present throughout the vertical extent of skarn. Systematic mineral compositional patterns include outward increase in hedenbergite + johannsenite components in clinopyroxene (<2 to >20 outward), increse in Sb+Bi contents of galena, initial increase followed by decrease in Mn contents of sphalerite (range from <.2% to >1% Mn), and an initial increase with outward variable increase and decrease in FeS contents of sphalerite (range of <3 to >20% FeS). Previously published sulfur isotope data is compatible with outward decrease in sulfur isotope ratios. Published isotope data combined with temperature estimates from phase homogenization and arsenopyrite-sphalerite geothermometry show a systematic decrease in temperature from the skarn-sulfide pipe center (>425 °C) to the margin (<300°C).

Comparison of stope maps to isotherm cross-sections indicates the bulk of mined sulfides were from areas surrounding the pipe core, in which temperatures declined from approximately 375°C to 300°C.

by techniques such as minor element distribution (Hall et al., 1971), sulfide phase homogenization (Czamanske and Hall, 1975) and fluid inclusion systematics (Rye et al., 1974). Based on their study, Rye et al. (1974) concluded that the Darwin Pb-Zn-Ag mineralization was deposited under near-isothermal conditions at a temperature of 325°C, by magmatic fluids flowing out of the adjacent, unmineralized, mesothermal Darwin stock. Rye et al. (1974) concluded that ore depostion took place due to pH increase at constant fO_2 and temperature, caused by fluid reaction with carbonate rocks; they noted horizontal zoning of S-isotopic values away from the Darwin stock. Rye et al. (1974)'s study may have contributed to a frequently-held notion that skarns can be relistically modeled as essentially isothermal deposits with mineralization controlled by pH changes.

Although widedly quoted in the isotopic literature, there are several features of the Darwin study as presented by Rye et al. (1974) which invite scientific scrunity: (1) S-isotope derived temperatures are generally 50-80°C higher than those determined by other techniques (Czamanske and Hall, 1975), (2) the Darwin quartz monzodiorite, with probable solidus temperatures >800°C, is located <50 m from the sulfide deposits, (3) the Darwin pluton is unmineralized and virtually unaltered (Hall and MacKevett, 1962; Newberry, 1987), and (4) the Darwin Pb-Zn-Ag-W metal assemblage is uncommon in skarns (Einaudi et al., 1981). There are also problems with the relative timing of plutonism and Pb-Zn-Ag ore deposition: the 174 Ma (U/Pb, Chen, 1977) Darwin stock is cut by the Davis thrust (Eastman, 1980; Newberry, 1987), with movement dated at 154-148 Ma (Dunne et al., 1987), but Pb-Zn-Ag mineralization cuts across the thrust and hence post-dates thrusting (Hall and MacKevett, 1962; Eastman, 1980) and must be at least 20 Ma younger than the supposed related pluton. Finally, the garnet >>pyroxene, high Ag-Te, and galena>sphalerite mineralogy of the Darwin deposit (Hall and MacKevett, 1962) is atypical of Pb-Zn skarns (Einaudi et al., 1981).

Newberry (1987) resolved some of these apparent conflicts by showing that there are three different plutonic suites associated with three different metasomatic skarn suites in the Darwin district. Newberry (1987) further showed that the contact-type W skarns were associated with the Darwin stock and that the vein-related Pb-Zn-Ag skarns were associated with younger quartz porphyry bodies. Supporting geologic data includes the presence of Pb-Zn skarns along faults which cut across and offset the Darwin stock (Figs. 1, 2) and granite porphyry and breccia bodies (Fig. 2) which intrude the Darwin stock and contain clasts of W-bearing, but Pb-Zn-poor skarn. Newberry (1987) suggested that the Pb-Zn-Ag-W ore assemblage may have resulted from superimposition of Pb-Zn skarns on an older W-skarn system.

This study was prompted by the need to reconcile the apparent contradition between isotopic studies of Rye et al. (1974), which concluded that mineralization was zoned around and caused by the Darwin stock, and petrologic-geologic studies presented in Newberry (1987), indicating that mineralization is unrelated to the Darwin stock. As there are no published maps for the deposit in which the skarns are distinguished or described and because pyroxene-rich skarns--so characteristic of Pb-Zn skarns (Einaudi et al., 1981)--have not been reported from the Darwin area, the investigation began with systematic surface and underground mapping and core logging. Because

Rye et al. (1974) had stressed the horizontal zoning of ores and sulfur isotopic ratios around the Darwin stock, a further investigation of zoning--based on ore and calc-silicate mineralogy, mineral compositions, and metal ratios--was undertaken. Given the new results from zoning studies, Rye et al. (1974)'s sulfur isotope model was re-interpreted. The zoning data reported herein is most consistant with a series of subvertical skarn pipes and related bedded skarns and veins, centered 100-300 m W of--and genetically unrelated to--the Darwin stock. The sulfur isotopic data is consistant with a model of fluid flow through and away from these pipes.

General Geology

Darwin area regional geology is summarized in Dunne et al. (1978) and Stone et al. (1989). Upper Paleozoic deep water sedimentary rocks (Stevens, 1986), largely carbonate turbidites (Stone, 1984) in the immediate Darwin mine area, were deformed into broad folds, probably associated with deformation underneath the nearby late Triassic Last Chance thrust fault system. As the upper plate of this fault (now eroded in the immediate Darwin area) was probably several km thick, significant overthickening of the stratigraphy took place. Rocks of the Darwin area were subsequently intruded by mid-Jurassic alkaline plutons (including the 174 Ma Darwin stock, Chen, 1977) and calc-alkaline granite plutons (including the 156 Ma Coso batholith, Chen, 1977)to the W of the alkalic plutons. A 4-6 km depth of emplacement has been suggested for the calc-alkaline plutons (Sylvester et al., 1978). Contact metamorpic recrystallization of the impure carbonate rocks caused a zone of idocrase-wollastonite calc-silicate hornfels, garnet-rich skarnoid, and bleached marble to be formed around the Darwin stock (Fig. 2; Hall and MacKevett, 1962; Eastman, 1980; Newberry, 1987). Tungsten-bearing skarns are locally present along contacts of the more differentiated units of the Darwin stock with the surrounding carbonate-bearing rocks, distributed symmetrically around the Darwin stock (e.g., Fig. 2; Newberry, 1987). Thrusting along the Davis fault system (Fig. 1), took place at 154-148 Ma (Dunne et al., 1978), and resulted in 1-3 km of E displacement of the upper plate, juxtaposing the Coso batholith and its adjacent Cu-skarns with the Darwin pluton and its adjacent W-skarns (Newberry, 1987) and telescoping the contact metamorphic rocks. Subsequent to thrusting, a series of granite porphyry dikes and breccia pipes (Fig. 2) intruded the metamorphic and igneous rocks along the NW margin of the Darwin stock; aplite geobarometry indictes these rocks crystallized at a pressure of approximately 0.5 kbar (Newberry, 1987). Pb-Zn-Ag skarns (restricted to the W side of the Darwin pluton) and Pb-Zn-Ag veins of the Darwin district formed along steeply-dipping faults--which are commonly marginal to the breccia bodies--and, less commonly, along granite porphyry dike contacts and along the Davis thrust (Fig. 2). Minor normal fault reactivation of the Davis thrust accompanying Cenozoic Basin-Range uplift (Dunne et al., 1978) caused slight deformation of ores in the vicinity of the thrust.

Investigative techniques

This study is based on underground (100 to 900 levels) and surface mapping of the Darwin mines at 1:2400, detailed logging of approximately 1000 m of diamond drill core, examination of approximately 300 polished and thin sections, approximately 450 microprobe analyses representing 80 thin sections and grain mounts, compilation of assay maps and drill assays, and sulfur isotope measurements for a galena-sphalerite pair and 2 galena samples. Mineral abundances were estimated using standard thin section point counting techniques. Electron microprobe analyses were performed using a 9-spectrometer ARL microprobe at UC Berkeley (silicates), as described in Newberry (1987), and a 3-spectrometer Chimeca microprobe at Washington State University (sulfides), as described in Meinert (1987). Mineral standards were employed and each analytical point represented the average of at least 3 analyses. Sulfide mineral separates were analyzed for sulfur isotope ratios by Krueger Enterprises, Cambridge, Mass. Data from petrographic and microprobe analyses were plotted on mine cross-sections; different projections for the petrographic, metal ratio, and microprobe data were employed to minimize projection distance, to best compare the results of this study to those of Rye et al. (1974), and to illustrate the three-dimensional character of the Essex ore body. Mine assay data, production data and drill hole assay data was compiled onto level maps, averaged into 10 m (minimum) blocks and ratiod Ratios were then projected onto mine cross-sections.

The Essex ore body (Fig. 2) of the Darwin deposit was selected for intensive study because all levels were accessible for underground mapping (courtesy of the Anaconda Company) and because well-located sample collections from this orebody were available at Stanford University.

PRESENT INVESTIGATION

Geology of the Darwin Pb-Zn-Ag skarns

Pb-Zn-Ag skarns of the Darwin deposit occur predominantly as skarn veins and bedded replacements (Hall and MacKevett, 1962; Eastman, 1980). There are in addition, at least two major pipe- (or chimney-) like ore bodies, the Defiance and Essex pipes. The Essex pipe is an irregular body elongated to the NW-SE and plunging at about 70° to the SW. Its shape is controlled by intersections of the N65°W Essex fissure zone with receptive carbonate units near the hinge zone of the doubly-plunging, N30°W-trending, Darwin antiform. Major "bedded" skarn zones are also present adjacent to the main pipe in marble beds immediately underlying sills of the Darwin pluton. This is especially the case in the upper levels of the mine and probably gave early workers the misleading impression that skarns were zoned away from the Darwin pluton. The varible shape of the Essex pipe is shown on Figure 3, a series of plan level maps with the extent of skarn at each level.

Fig. 4 shows a simplified map of the Essex pipe area on the 600 level illustrating the structural and stratigraphic controls on skarn formation. Narrow skarn and/or sulfide veins are present in calc-silicate hornfels; the bulk of skarn appears to replace marble. Unreplaced marble is sometimes present between skarn and the Darwin pluton (Fig. 4), confirming that these skarns are younger than the pluton. Sulfides occur disseminated throughout the skarn, in minor veins in the skarn, as occasional through-going veins and as "bedded replacements" distal to the skarn. Pyroxene-rich skarns are present in the Essex pipe at the 600 level and below; they are rarely in contact with marble and are typically surrounded by garnet skarn.

Lateral and vertical zoning in the Essex pipe is illustrated by a vertical cross-section (Fig. 5) constructed at approximately right angle to the NW-SE elongation of the pipe (Fig. 3). The Essex pipe contains sub-equal amounts of pyroxene and garnet-rich skarn at depth; pyroxene skarn is both cut across and vertically supplanted by garnet-rich skarns. Garnet-rich skarns are in metasomatic contact with marble throughout the pipe, showing no evidence of replacing pyroxene-rich skarn at the marble contact. Skarns cut across and replace calc-silicate hornfels and skarnoid beds and form laterally extensive replacement bodies in marble and hornfels adjacent to the pipe (Fig. 5). In many cases the light-colored, grandite garnet skarns could not be easily distinguished from the light-colored, idocrase-garnet hornfels during underground mapping and AX core logging; most of these contacts are probably gradational. Rocks identified with certainty as skarn during underground mapping and core logging were dominated by coarse-grained garnet ± pyroxene with accessory sulfides and/or contained obvious garnet veins.

With increasing vertical height, sulfide-bearing veins--which cut across skarn--are common, however skarns are present throughout the entire vertical exposure of the Essex pipe. Coarse grained garnet-galena skarn--showing no evidence for garnet destruction-- outcrops as the surface expression of the Essex pipe (Fig. 2) and sulfides mostly occur as disseminations in the skarn below the 500 level. Occasional, massive quartz-carbonate-sulfide bodies are present as replacements of marble adjacent to skarn (Fig. 5); cross-cutting relations indicate that these bodies were formed after the skarns. Although sulfides, expecially galena, commonly enclose or fill vugs and fractures in skarn minerals, unaltered garnet is present adjacent to sulfide throughout the pipe. Galena veins with coarse-grained, unaltered garnet margins also occur from the deepest levels of the mine to the surface. Very late mineralization consists of calcite-pyrite "fissures", especially common along lithologic contacts and faults. These veins have low economic metal values, but contain spectacular pyrite and calcite crystals.

The Defiance pipe is a steeply-dipping body present 700 m SE of the Essex pipe (Fig. 2). This part of the Darwin deposit is currently accessible only at the 400 and 570 levels, and consequently it was less-well studied. On the 400 level it contains quartz, carbonate, bustamite, garnet, and retrograded pyroxene with massive to disseminated sulfides. Limited logging of AX drill core indicates that garnet-pyroxene skarns are present at deeper levels. Drill core also shows that a small body or bodies of granite porphyry (with quartz-K-feldspar veinlets), porphyry-matrix breccia, and skarn-matrix breccia (which contains galena and sphalerite) occurs below the 1000 level. The granite porphyry and porphyry-matrix breccia are surrounded by galena-sphalerite-bearing skarn. Above the 400 level the pipe horsetails into several quartz-carbonate sulfide veins which lie along the bedding of, and partly replace, garnet skarn (Hall and MacKevett, 1962; Fig. 2).

Skarn Mineralogy

The mineralogy of the Darwin Pb-Zn-Ag skarns is relatively simple, although there are complex mineral compositional patterns. The most abundant mineral is grandite garnet, with compositions ranging from 100% to 5% andradite (Fig. 6). Four generations of garnet have been identified, based on optical and compositional properties (Figs. 6, 7). Garnet generations were identified on the basis of overgrowth textures and rare vein relationships. Several garnet types are typically present in the same sample and in many cases, 3 generations are present in the same grain (Fig. 7a).

The earliest garnet (generation 1) possesses "blotchy", irregular birefringence and typically occurs as cores to later garnet types. These garnets have compositions of Ad_{60-92} with 1% spessartine and show systematic enrichment in andradite component from core to margin. Blotchy birefringent garnets are surrounded by a narrow rim of yellowish, isotropic (generation 2) garnet with compositions of Ad_{96-100}. Andradite garnet commonly exhibits incipient alteration to very fine-grained opaques. The next (third) generation of garnet is "banded birefringent", essentially identical to the DBB garnets of Capote Basin described by Meinert (1982). This generation (Fig. 7a) is characterized by narrow (.01-.002 mm) bands of alternating birefringent and nearly isotropic garnet, with alternating high and low iron contents. These garnets have compositions of Ad_{94-66} with 1-2% spessartine. The final (fourth) garnet generation is yellow and evenly birefringent. This garnet occurs as the final rims on banded birefringent garnets and more rarely as isolated grains in upper levels of the mine (Fig. 7b). These garnets have compositions of Ad_{65-5} with a systematic rimward decreasing iron trend. Lowest-iron, evenly birefringent garnets also contain 5-7% spessartine component.

Garnets show complex relations with sulfides. Initial sphalerite and galena deposition apparently post-dated third generation banded birefringent (bb) garnet, as these sulfides commonly occur filling vugs between adjacent bb garnets, and never as inclusions within these garnets. The bb garnets adjacent to interstitial sulfides show no signs of alteration--suggesting sulfides were stable with these garnets--but andradite cores to the bb garnets commonly exhibit incipient alteration (Fig. 7c). Isolated grains of andradite garnet are commonly replaced by sulfides + quartz + calcite, even in deeper levels of the mine (Fig. 7d). Late, evenly-birefringent, grossular-spessartine garnets, on the other hand, were deposited contemporaneously with sulfide in many cases; for example, as tiny (05 mm) garnets intergrown with sulfide, magnetite, quartz, calcite, and bustamite in the Defiance pipe (Fig. 7b). These late garnets are also present as envelopes around galena veins in calc-silicate hornfels. Garnet of all types is strongly altered--typically to fine-grained, chlorite-calcite-epidote-magnetite-pyrite--where adjacent to calcite-pyrite fissures.

Pyroxenes are much less common than garnet in presently known exposures of the Darwin skarns, and unlike garnet, pyroxene deposition probably predated the bulk of sulfide deposition. Massive pyroxene skarns, only currently known below the 500 level of the Essex pipe, contain 0.5 to 2 cm long, bladed pyroxenes, partly replaced by garnet and sulfides (Fig. 7e). Pyroxene has not been identified in the Essex pipe Pb-Zn skarns above the 3A level, either because it has been totally replaced by garnet ± sulfide or more likely, because it ever formed in the upper portions of the Essex pipe. In contrast, the Defiance pipe (400 level) contains small clots of isolated pyroxene grains (with similar optical orientations) surrounded by murky carbonate + sulfide; this may indicate extensive retrograding of an originally pyroxene-rich skarn pipe.

Below the 600 level in the Essex pipe, pyroxenes show core to rim iron enrichment; above the 600 level they generally show rimward iron depletion. Rare, late pyroxenes, occurring with the evenly birefringent yellow garnets, are nearly pure diopside. Pb-Zn skarn-associated pyroxenes show a narrow range of compositions, Di_{70}-Di_{100}, with sub-equal and co-varying Mn and Fe contents (Fig. 8)

Other non-sulfide minerals in the Pb-Zn skarns occur in several different modes. Fluorite (especially common in upper parts of the mine) and k-feldspar are sporadically present in garnet-defined vugs. Wollastonite is common in the calc-silicate hornfels, but is typically retrograded to fine-grained quartz + calcite where near Pb-Zn skarn skarn veins. Idocrase is also common in the hornfels, is present in some Pb-Zn skarns (remnant metamorphic grains?) and occurs in small amounts with bustaminte, quartz, calcite, and grossularitic garnet in the Defiance pipe. Epidote, chlorite, and actinolitic amphibole are common in the uppermost parts of the mine, resulting from retrograde alteration of garnet and pyroxene.

As discussed in Czamanske and Hall (1975), the ore mineralogy at Darwin is dominated by sphalerite and slightly argentiferous galena. Galena in the upper parts of the mine is more Ag-Sb-Bi-Se rich and contains exsolved sulfosalts. Late carbonate-quartz-sulfide veins, with a poorly-characterized distribution, contain tellurium-rich minerals, sulfosalts, and native gold. Pyrite is common in all the ore types except the last; its paragenesis is commonly early relative to galena. Pyrrhotite occurs in the western part of the Essex orebody, approximately 200 meters from the main Darwin stock contact (as measured along cross-section E-E', Fig. 2). As noted by Eastman (1980), pyrite-pyrrhotite relations are complex in the W part of the Essex zone, with a paragenesis of (1) early pyrite, (2) hexagonal pyrrhotite, (3) pyrite + galena + sphalerite ± magnetite, (4) monoclinic pyrrhotite + "porus" pyrite. Chalcopyrite is noticably present in deeper portions of the deposit; tetrahedrite-tennantite and arsenopyrite are also present in small amounts. Other rare and trace minerals are described by Czamanske and Hall (1975).

Mine-scale zonation patterns

METAL ZONING--GENERAL FEATURES

Metal zoning studies in the Darwin mines are complicated by the fact that assays and production statistics reflect a combination of skarn, vein, and supergene-enriched ores. Ratios above the 3A level mostly reflect supergene enrichment and not the hypogene pattern. Despite these problems, metal distribution in both the Defiance and Essex areas shows both vertical and horizontal zoning compatible with a pipe morphology for both the Essex and Defiance orebodies.

Vertical zoning (Table 1) is shown by Anaconda company sampling of slightly mineralized hornfels in the Essex zone. By sampling a consistant lithology, and avoiding both coarse-grained skarns and large veins, the data reflect the gross metal pattern. Due to limited sample density, however, 3-dimensional analysis, of the data is not meaningful. The metal concentrations and ratios present define generally restricted values for lower, upper, and middle regions of the Essex area, with less systematic variation seen within these three regions. Lack of better vertical trends is due to the presence of both horizontal and vertical zoning. In a general way, average ratios of Pb/Zn, Pb/Cu and Ag/Pb do rise with elevation, as do absolute concentrations of Bi. The abundance of W and As generally falls with increasing elevation, and Mo shows an irregular pattern. The relatively high Ag/Pb ratio seen at the lowest level indicates that some Ag occurs with chalcopyrite and tennantite (Hall, 1971) as well as with galena and Pb-sulfosalts (Czamanske and Hall, 1974). The overall increase in Ag/Pb with height, however, is in agreement with previous studies showning an increase in Ag-sulfosalts with height in the mines (Czamanske and Hall, 1974). The increase in W with depth probably reflects the tendancy for scheelite deposition at relatively high temperatures and at an early stage in the paragenesis (Hall and MacKevett, 1962; Eastman, 1980). The general rise in Pb/Cu, Pb/Zn, and Ag/Pb with elevation indicate a strong vertical component to hydrothermal fluid flow.

METAL ZONING--ESSEX PIPE

Combined horizontal and vertical zoning in the Essex pipe is illustrated by metal ratio cross-sections. Figure 9 (a,b) shows metal zoning along E-W section B-B′ and Figure 9 (c,d) shows metal zoning along N-S section CC′ (both located on Fig. 2). Metal zoning in both cases is complicated by the presence of several different ore types, but the ‘inverted cup’ zoning suggests a pipe morphology to the mineralization, as indicated by Figure 5. Also, the inverted cup zonation in the two perpendicular cross-sectional views indicates that the mineralization does have 3-dimensional pipe morphology.

Metal zoning in the Essex skarn (Fig. 9) can be explained by an outward and upward change from sphalerite- galena-rich skarn, similar to that observed in other lead-zinc skarns (e.g., Einaudi et al., 1981; Yun and Einaudi, 1982; Shimizu and Iiyama, 1982; Meinert, 1987; Megaw et al., 1988). An outer fringe the pipe has relatively low Pb/Zn and represents py-(or po-) rich mineralization low in both Pb and Zn, and results in the cup-like form to the metal ratio contours. Similar outward changes in Pb/Zn ratios have been observed and described theoretically by Loucks and Peterson (1988).

The zoning in Ag/Pb--which generally increases outward and upward from the pipe center--may be caused by the fact that paragenetically younger galena contains more Ag (Hall, 1971; Czamanske and Hall, 1975) and this galena tends to occur around the periphery of the pipe. A possible explanation for the very high Pb/Zn and Ag/Pb ratios seen east of the central pipe area is that late sulfide veins tend to be concentrated in this area. Variable Ag/Pb zonal patterns are seen in other Pb-Zn skarns and mantos: Gilmer et al. (1988) show an outward decrease, Rubin and Kyle (1988) show an outward increase and Megaw et al. (1988) show an overall outward increase followed by a decrease.

Within the Essex pipe, The high-grade ore stopes are in areas with high Ag/Pb and Pb/Zn ratios, hence there was a limited tonnage of rock mined--especially below the 400 level--and many stopes were localized in the area between the skarn pipe center and the Darwin stock and in the uppermost part of the skarn pipe center. Although not previously noted, stope cross sections do outline an "inverted cup" morphology to the Essex orebody (c.f., Czamanske and Hall, 1975, fig. 1).

METAL RATIOS--DEFIANCE PIPE

Metal ratios for the Defiance pipe cross-section below the 400 level (D-D', Fig. 10), indicate a Zn/Pb and Pb/Ag-rich core, with Pb and Ag increasing outward and then diminishing somewhat, although the Pb/Zn and Ag/Pb ratios for the fringe mineralization is greater than in the center of the pipe. High values for Pb/Zn above the 400 level probably reflect supergene enrichment. The metals are clearly zoned around a small granite porphyry body, ✓ which in turn is surrounded by low-sulfide skarn-matrix breccia than then by mineralized skarn. Much of the ore from the Defiance pipe came from a near-vertical replacement body between the 900 and 400 levels (Hall and MacKevett, 1962) located west of and above the Defiance pipe center. The metal zoning data, combined with examination of AX drill core from the lower Defiance mineralization, suggests that the Defiance pipe is similar to, but more deeply-seated than, the Essex pipe.

MINERAL ZONING--ESSEX PIPE

Mineral zonation in the Essex pipe is most noticable for the sulfide minerals. A cross-section through the Essex skarn zone, Fig. 11, shows several types of mineralogical zoning around the central skarn pipe defined by geologic mapping (Figs. 3,4,5) and metal ratio studies (Fig. 9).

Galena/sphalerite ratios in skarn, based on underground mapping, core logging, and handspecimen and polished section examination (Fig. 11a) show the pipe has a zinc-rich core and a lead-rich periphery. Galena/sphalerite ratios are not clearly defined on the margins of the skarn, where abundances of both these minerals are low relative to pyrite and pyrrhotite, and the relative proportions of galena to sphalerite might be low on the fringes of the pipe. These mineralogical ratios are consequently in large agreement with the Pb/Zn ratios defined by ore grades. The more economic zones in the mine are defined by high sulfide abundance together with high galena/sphalerite ratios; these are generally found in the upper parts of the deposit where there are also galena/ sphalerite ratios of 0.5-3.

Sphalerites in the Essex pipe skarn commonly contain very fine-grained, subhedral, and oriented chalcopyrite grains, similar to "chalcopyrite disease" seen in Kuroko deposits (Barton, 1978; Eldridge et al., 1983). Estimated modal abundances of chalcopyrite in sphalerite and chalcopyrite (as isolated occurrences) outline a copper-rich "spine" (Fig. 11b) to the orebody. Hall (1971) presented data for Cu contents of sphalerites; these also outline a copper-rich core to the orebody. These Cu data are also consistant with limited Cu assays, for which values up to 0.65% Cu are identified in deeper parts of the mine.

Sphalerite color, which partly reflects variations in combined iron, manganese, and cadmium content of sphalerite, changes within the ore zone: sphalerites in the deeper, more central, and west-peripheral parts of the mine are darker-colored, whereas sphalerites in upper and east-peripheral parts of the skarn are more pale-colored (Fig. 11c).

Paragenetic studies of galena-sphalerite relationships, based on veining and inclusion textures in polished section, indicate a central zone with complex paragenesis and likely multiple periods of ore mineralization, and a peripheral zone dominated by the simple paragenesis of sphalerite replaced or followed by galena (Fig. 11d). This paragenetic zoning is consistant with Hall and MacKevett (1962) and Eastman (1980), who report galena generally younger than, but commonly overlapping with, sphalerite. Lowermost parts of the Essex pipe also generally contain a simple paragenesis of sphalerite followed by galena.

Pyrrhotite is sporadically present in the west part of the Essex orebody and the contact between pyrrhotite-bearing and pyrrhotite-absent assemblages roughly parallels the main Darwin stock contact (Fig. 11e), as noted by Rye et al. (1974). Within the pyrrhotite-bearing zone, however, there is no apparent trend to the abundance of pyrrhotite inclusions in sphalerite. The origin of these pyrrhotite inclusions is unclear: they could concievably represent epitaxal growth (but differences in crystal structure between sphalerite and hexagonal pyrrhotite make this unlikely), and are unlikely to represent simple exsolution due to different sulfur/meltal ratios in sphalerite and pyrrhotite. More likely they represent de-sulfidation "exsolution", as represented by an equation like

$$\mathrm{FeS\ (in\ spl)} \rightarrow \mathrm{Fe_{1-x}S} + x/2\ \mathrm{S_2}$$

and suggest that relative sulfur fugacity fell after deposition of these sphalerites.

The distribution of fine-grained pyrite inclusions in sphalerite is more regular, as there apprears to be a core zone in the upper parts of the Essex orebody which contains a high abundance of inclusion pyrite (Fig. 11f). Inclusion pyrite probably represents sulfidation "exsolution" of sphalerite as represented by

$$\mathrm{FeS\ (in\ spl)} + 1/2\ \mathrm{S_2} \rightarrow \mathrm{FeS_2},$$

as a "charcopyrite disease"-like replacement of sphalerite by pyrite is ruled out by the major difference in crystal structures of pyrite and sphalerite. The presence of both sulfidation and de-sulfidation reactions suggest complex changes in fluid chemistry with space and time and are reflected in complex sphalerite compositional patterns (see ahead).

Non-sulfides also show systematic patters around the skarn pipe core. Zoning of garnet generations present (c.f., Fig. 7a) shows a systematic horizontal and vertical pattern (Fig. 11g). The earliest garnet generation is characteristic of the lowermost skarn in the Essex pipe with the youngest generation garnet characteristic of the upper and upper-peripheral parts of the skarn. The central skarn spine is outlined by garnets with final banded birefringent rims, and yellow birefringent garnet chracterizes the upper parts of the Essex pipe away from the central core (Fig. 11g).

Unreplaced marble beds are common away from the Essex skarn pipe and some are between the skarn and the Darwin stock (Figs. 4,5). These marbles commonly contain fine-grained, disseminated graphite away from the Darwin stock and are bleached close to the stock (Fig. 11h). The distribution of bleached and un-bleached marble relative to the Darwin stock contact is compatible with bleaching during intrusion of the Darwin stock; subsequently overprinted by the Pb-Zn skarns. Eastman (1980) noted that graphite is variably presently in the Essex *skarn*, but restricted to a zone located> 150 m west of the main Darwin stock contact. The similarity in occurrence of unbleached marble (Fig. 11h), graphite in *skarn*, and pyrrhotite-bearing ores (Fig. 11e) suggests that progressive reduction of the ore fluid by reaction with organic matter in the carbonate rocks is related to pyrrhotite and graphite deposition in skarn.

K-feldspar is a trace constituent in the skarn, usually present filling vugs between garnet grains and present in textural equilibrium with sulfides and fluorite. Presence of unaltered K-feldspar throughout skarn below the 400 level (Fig. 11h) indicates that fluids below the 400 level were consistantly at a pH above muscovite stability Fine-grained, texturally late, muscovite-quartz alteration of the skarn K-feldspar is erratic, but limited to the uppermost part of the orebody, above the 400 level (Fig. 11h). A similar pattern is seen for chlorite-calcite-iron oxide alteration of garnet and for bustamite alteration of pyroxene (Fig. 11h), which are both concentrated at the top and periphery of the Essex orebody. These patterns indicate lower-temperature (lower pH?), post-skarn alteration concentrated in the upper and peripheral parts of the system and suggest that conditions consistantly stayed within garnet stability in the lower-central parts of the skarn pipe.

In summary, distribution of minerals and textures in the Essex pipe indicates a systematic zoning around a core zone and a broad vertical zoning, both consistant with the geologic mapping. The mineral parageneses and zonal patterns suggest that multiple mineralization events took place. Except for the distribution of pyrrhotite (which may represent pre-Pb-Zn skarn bleaching of marbles by Darwin stock-related fluids), there is no suggestion that the skarns and skarn-related ores are zoned around the Darwin stock.

MINERAL COMPOSITION ZONING--ESSEX PIPE

Due to the highly complex zoning of individual garnets (Figs. 6, 7a), the deposit-wide zoning of garnet compositions is also highly complex. Given the range of garnet compositions observed in a single grain, "average" compositions show no recognizable patterns. The restriction of the second generation yellow isotropic garnet to lower portions of the Essex skarn pipe, however, (Fig. 11g) indicates that andradite garnet *per se* is restricted in distribution, and is only abundant in lower parts of the Essex pipe.

Pyroxene compositions in terms of maximum hedenbergite (Hd) + Johannsenite (Jo) contents show a simpler pattern (Fig. 12a): pyroxenes in the deeper and core part of the orebody are very diopsidic and maximum Fe +Mn contents increase progressively away from the core zone. Progressive increase in (Fe+Mn)/Mg ratio of clinopyroxenes away from the fluid source has been documented for other Pb-Zn skarns (e.g., Einaudi and Yun, 1982; Meinert, 1987), consequently the Essex pipe pyroxene data point to a central skarn spine some 100-300 m W of the Darwin stock. The low maximum Fe+Mn contents of the lowest, central pyroxenes suggest they are not far from the fluid source.

Galena compositions also show a zonal pattern (Fig. 12b). Sb+Bi contents of galenas, taken from Czamanski and Hall (1975) and Hall (1971) indicate a core of low-Sb+Bi galenas surrounded by a periphery of higher Sb-Bi galenas. This zoning, similar to the progressive enrichment in Fe-Mn contents of pyroxenes by selective Mg-depletion (Einaudi et al., 1981), may be caused by preferential removal of early-stage (Czamanske and Hall, 1975) Sb-Bi-poor galena.

Manganese contents of sphalerites are also zoned (Fig. 12c), but show an initial upward and outward increase from the deep center of the pipe and a return to low Mn contents at the fringes of the pipe. This pattern bears some similarites to the Mn in pyroxene pattern (Fig. 12a) in terms of the initial outward increase in Mn; lower temperatures on the fringe of the pipe (see ahead) may restrict MnS solubility in sphalerite, causing the low Mn characteristic of the skarn fringe.

Distribution of mole % FeS in sphalerite is complicated by the presence of "exsolved" pyrite and pyrrhotite (c.f., Fig. 9e,f). Iron contents performed on high-quality sphalerite separates (Hall, 1971) automatically include the "exsolved" iron sulfides, but microprobe analyses must be corrected for the abundance of these iron sulfides. Re-integration of this iron, as described by Eastman (1980) generally results in small increases in the calculated FeS content, and is quantitatively important only in those areas with >5% iron sulfide in the sphalertite.

The distribution of calculated mole % FeS in sphalerite is the only mineraly compositional pattern showning partial assymmetry around the skarn core (Fig. 12d). There is a general increase in mole % FeS moving upward and around the pipe (Fig. 12d) although increases in FeS from the core towards the pluton are much smaller than those from the core away from the pluton. Additionally, a zone of lower-iron sphalerites appears in the uppermost levels of the Essex pipe. Lack of strong correlation between iron contents in sphalerite and color is evident in comparing Fig. 9c to Fig. 12d; this effect has been noted by other workers (e.g., Scott and Barnes, 1972) who suggest that excess sulfur can also cause sphalerite darkening.

FeS contents of sphalerite increase with decreasing sulfur fugacity, so that high FeS contents in sphalerites to the W of the pipe reflect the lower-sulfur fugacity conditions which caused pyrrhotite occurrence. Sphalerite with more than 20 mole % FeS is only present where pyrrhotite occurs, reflecting equilibrium between sphalerite and fluid. Sphalerites with less than 20% FeS also occur within the pyrrhotite zone, however, indicating that sufur fugacity fluctuated with time, sphalerite re-equilibrated with monoclinic pyrrhotite (both suggested by Eastman, 1980), and/or sphalerite-fluid equilibrium was not maintained. Increses in FeS content of sphalerite from the pipe center towards the Darwin stock and from deep in the pipe upward indicate sulfur fugacity increased upward and outward in all directions from the lower center of the pipe. Although the pattern is complicated by very low sulfur fugacity conditions away from the Darwin stock, the central skarn "spine" is still apparent in the FeS contents of sphalerites. Uppermost low-iron sphalerites reflect an increase in sulfur fugacity which is spatially coincidental with the locus of extensive retrograde alteration of garnet and pyroxene (Fig. 11h) and consequently, may be related to fluid cooling.

MINERAL COMPOSITIONAL ZONING--DEFIANCE PIPE

Limited data for mineral compositions from the Defiance pipe (Fig. 13) is compatible with the model developed for the Essex pipe. Iron + manganese contents of pyroxenes increase upward and outward, as do Bi+Sb contents of galena. Pyroxene compositonal isopleths compare nicely to the pipe outline defined by metal zoning and are symmetrically distributed above the granite porphyry plug. Sphalerite shows virtually no compositional variation, however, indicating minimal changes in relative sulfur fugacity despite major changes in pyroxene compositions.

SULFUR ISOTOPE RATIO ZONING

Rye et al. (1974) presented sulfur isotope data for the Darwin deposit, which they used to estimate a mineralization temperature of 325°C and describe a fluid flow pattern away from the Darwin stock. Rye and Ohomoto (1974) show zoning of del ^{34}S for sphalerite, which can be interpreted as zoning around a central core; Fig. 14a shows zoning of del ^{34}S for galena (employed because Rye et al.,1974, present a wider distribution of galena than sphalerite data).. Figure 14a also includes 3 values determined for this study by Kruger Enterprises. Values for del ^{34}S of galena (Fig. 14a) can be interpreted as indicating zonation around that same skarn pipe center which was defined by mineral, metal, and mineral compositional zoning (Figs. 5,9,11,12). Values of galena del ^{34}S are highest in the central, deep part of the pipe and decrease outward and upward (Fig. 14a), although the core-to-margin zoning is greatest on the W side of the pipe.

In contrast to the pattern for the Essex pipe, sulfur isotopic ratios from the Defiance pipe show only minor variations (Rye et al., 1974). Values decrease upward in a relatively systematic manner, e.g. pyrite del ^{34}S changes gradationally from 4.4 permil at the 1200 level to 2.0 permil near the surface. The available data are insufficient to define a horizontal zonation.

THERMAL ZONING

Temperatures derived from S-isotope fractionation (Rye et al., 1974), trace element distribution in sulfides (Hall et al., 1971), phase hogomenization (Czamanske and Hall, 1975), and arsenopyrite geothermometry (this study) are all are compatible with thermal zoning around and above the Essex pipe. Values shown in Fig. 14b have been taken from Rye et al. (1974), and Czamanske and Hall (1975). The values shown have been edited by (1) averaging temperatures defined by galena-sphalerite and galena-pyrite thermometry where the two differ by more than 80°C (Rye et al., 1974, showed that the two were usually similar) and (2) not presenting those values for which gross disequilibrium was demonstrated (following Rye et al., 1974). An additional temperature was determined from a sphalerite-galena pair analyzed for this study. Also shown are temperatures defined by Mn distribution between sphalerite and galena (Hall et al., 1971) and locations of samples for which sulfosalt inclusion homogenization experiments indicated formation temperatures in excess of 350°C (Czamanske and Hall, 1975).

Three additional temperatures plotted on Fig. 14b were estimated from microprobe compositions of co-existing pairs of sphalerite and arsenopyrite grains. Temperatures were estimated using the intersections of arsenopyrite isopleths (Kretschmar and Scott, 1976) with sphalerite isopleths (Scott and Barnes, 1971) on a log fS_2 vs.

temperature diagram. Table 2 gives the sulfide compositions and estimated temperatures.

Despite the variety of techniques employed, all temperature estimates give values in excess of $350^{\circ}C$ in the skarn pipe core and temperatures $<300^{\circ}C$ marginal to the skarn core (Fig. 14b). There appears to be a small vertical thermal gradient and a large horizontal thermal gradient.

Temperatures determined by S-isotope fractionation from the Defiance pipe (Fig. 13) also indicate high temperatures ($>375\ ^{\circ}C$) for this skarn pipe. An anomalously low temperature ($295\ ^{\circ}C$) sample is located in a zone of major calcite-quartz-sulfide alteration (as indicated by underground mapping), whereas the other samples are from sulfide-bearing skarn (sample descriptions in Hall and MacKevett, 1962, pg. 69). Hence, the the higher and lower temperature samples reflect temperatures of skarn formation and skarn destruction, respectively, rather than a time-independent thermal zonation. As all the data are from the central part of the pipe or the "bedded skarn" extension (c.f., Hall and MacKevett, 1962), the data cannot resolve a horizontal thermal zonation.

DISCUSSION

Temperatures of ore deposition

Because Rye et al. (1974) assumed "that the general direction of movement of the hydrothermal fluids at Darwin was upward and outward from the quartz monzonite" and several of their lower temperatures were from samples close the the Darwin pluton, they viewed the S-isotope-derived temperature variations as largely due to uncertainties in the technique. They also concluded that earlier-derived temperature estimates based on trace element distributions (Hall et al, 1971) were approximately 50°C high due to large temperature extrapolations of the required K_d's. However, the trace element-derived temperatures show the same relative order as the S-isotope temperatures (Fig. 14b), indicating that the thermal zonation pattern is real.

Some of the differences between the isotopic and trace element - determined temperatures can be reconciled as due to isotopic fractionation. Rye et al. (1974) showed that sphalerite showed a systematic rimward decrease in del ^{34}S of 0.5 permil. Also, del ^{34}S of bulk samples from sphalerites differed by up to 0.5 permil from drilled sphalerite rim samples. Given that galena is typically younger than sphalerite (Hall and MacKevett, 1962; Eastman, 1980; this study) galenas only equilibrated with sphalerite rims. Data from Rye et al. (1974) shows rim samples yield temperatures 5-45°C warmer than bulk samples from the same sample material. Paragenetically, much of the galena is deposited simultaneously with pyrite (Eastman, 1980), so that pyrite-galena pairs might yield more appropriate temperatures. Comparison of calculated galena-sphalerite to galena-pyrite data (Rye et al., 1974) yield temperatures higher, on average, by 20-30°C for the former. These arguments suggest that the S-isotopic temperatures on Fig. 14b are probably low by about 20-30°C, and that temperatures in the skarn core were probably in excess of 400°C.

Partial isotopic re-equilibration is also possible, causing re-setting of all the values to lower temperatures, but preserving the original thermal distribution. Eastman (1980) showed that compositions of sphalerites in sphalerite-pyrite-pyrrhotite assemblages were anomalously iron-poor--indicating formation pressures in excess of 5 kb. Eastman (1980) concluded that these low contents were acquired when the (adjacent) original hexagonal pyrrhotite was altered to monoclinic pyrrhotite, as sphalerite in equilibrium with pyrite and monoclinic pyrrhotite has low iron contents (Scott and Kissin, 1973). Given this compositional re-equilibration, isotopic re-equilibration is likely to have taken place. Although such re-equilibration is only indicated for the pyrrhotite-sphalerite ores, it is possible that partial re-equilibration during continued fluid flow partly re-set many of the S-isotope determinations. If this was the case, it would suggest that temperatures for **initial** sulfide deposition are underestimated by as much at 50°C, a value required to make the S-isotope temperatures agree with other temperature estimates.

In addition to S-isotope fractionation uncertainties, however, reconciliation of the various <u>average</u> temperature estimates (377°C by minor element distribution, 325°C by S-isotope fraction, >350°C by phase homogenization) can be effected if a thermal zoning is recognized, with many of the higher <u>average</u> temperature estimates simply derived from sample sets representing hotter portions of the deposit. Perhaps average temperature in this context has little useful meaning.

Regardless of the precise temperatures, much of the sulfide deposition took place at temperatures in excess of at least 375^{o}C, and a strong lateral thermal gradient was present. At an X_{CO2} <.02 (computed by Rye et al., 1974), pressure <.5 kbar (indicated by aplite geobarometry, Newberry, 1987, and by 20% FeS sphalerite with pyrite-pyrrhotite; Hall and MacKevett, 1962), and oxidation state between hematite-magnetite and nickel-nickel oxide (see ahead), grandite garnet is stable to at least 350^{o}C (Taylor and Liou, 1978). This is consistant with much of the sulfide deposition with or in equilibrium with garnet skarn, as suggested by the petrographic data (e.g., Fig. 7b). Existance of a strong lateral thermal gradient (Fig. 14) indicates that sulfide deposition was not an isothermal process, as suggested by the variations in sulfide-silicate relations (e.g., Fig. 11h).

Conditions of Sulfide deposition and Deposit formation

Rye et al. (1974) explained the general decrease in S-isotope ratios of sulfides away from the Darwin stock by proposing that fluid pH increased (at constant oxidation state and constant temperature) in moving away from the stock, due to reaction with carbonate rocks. By this model, S-isotope ratios should uniformly decrease and iron contents of sphalerites (due to the increase in sulfur fugacity as the pyrrhotite-pyrite buffer is approached) should uniformly increase away from the Darwin stock. Other mineralogical and compositional patterns should presumably be similar. As discussed by Eastman (1980), Rye et al. (1974)'s model also requires maintanence of low pH's in ore solutions within 100 m of the Darwin stock despite the presence of unreplaced marble there (Figs. 4,5). As shown by Rye et al. (1974), the high salinities (>24% NaCl) of the ore fluids combined with a lack of evaporite units in the stratigraphy, indicate the fluids were of a predominantly magmatic origin--this does not indicate they came from the Darwin monzodiorite, however.

Utilyzing the sphalerite compositional pattern (Fig. 12d) from this study and S-isotope variations from Rye et al. (1974) and this study allows one to more quantitatively track solution characteristic changes in the Essex pipe (Fig. 15). Because H_2S K_a's cannot be extrapolated with confidence above 350°C, Fig. 15 is calculated for a temperature of 350°C; it is, in consequence, only strictly applicable to the margin of the core zone. Because the topology of the pH-log fO_2 diagram does not change appreciably with decreasing temperature (Ohmoto, 1972), this isothermal diagram can be applied to the deposit, with suitable adjustment for increasing fractionation factors at declining temperature.

Galena in the lower central part of the Essex pipe is with low-Fe sphalerite (Fig. 12D) and would have an isotopic compositon of approximately 1 permil if the parent fluid had a bulk isotopic composition of approximately 5 permil (1.5-2 permil for galena precipitating from a similar fluid at 450°C). Bulk fluid del ^{34}S of 5 permil is within the magmatic range for a relatively oxidized fluid (Ohmoto, 1979)--i.e., one co-existing with low-Fe sphalerite. As the pyrite-pyrrhotite-magnetite tripe point approximately corresponds to the NNO buffer at 450°C, the initial oxidation state of the fluids is between HM and NNO. The pH of the calculated ore fluid is at about that required for muscovite-K-feldspar-quartz stability (calculated for Darwin composition fluids by Rye et al., 1974), as geologic mapping shows the skarn-forming fluids interacted with micaceous hornfels units (Fig. 5) and deposited K-feldspar (Fig. 11h).

Fluids traveling up and to the E from the skarn pipe core followed a path of decreasing oxidation state and increasing pH, as indicated by sphalerite compositions (Fig. 12d) and S-isotope ratio variations (Fig. 14a) to neutral pH for that temperature (Fig. 15). Increase in pH is a logical consequence of interaction with carbonates, but the decrease in oxidation state is not. The fluids might be self-reducing, due to deposition of Fe^{3+}-rich garnet from Fe^{2+}-domiant fluids or deposition of pyrite (S^{-1}) from H_2S (S^{-2})-rich solutions. Additionally, fluids buffered by the assemblage garnet + pyrite, would be forced to lower oxidation states with increase in pH (Fig. 15), by following a boundary curve parallel to the magnetite-pyrite boundary.

Lower-iron sphalerites in the uppermost part of the pipe together with little change in S-isotope ratios requires both oxidation and pH <u>decrease</u> (Fig. 15). Decrease in pH is consistant with sericite-quartz alteration of K-feldspar in the upper part of the skarn (Fig. 11h). Rye et al. (1974) indicate that fluids resonsible for (late) cabonate deposition had a partial non-magmatic character; perhaps mixing of such fluids up the upward-rising skarn fluids resluted in oxidation. Oxidation could cause decrese in pH (especially at temperatures below 300°C) by partial conversion of the weak acid H_2S to the strong acid H_2SO_4.

Fluids flowing from the pipe to the west follow a path similar to the E-flowing fluids, but the high graphite content of the marbles to the W of the pipe causes a greater decrease in oxidation state. Buffering by garnet-pyrite during continued decrease in oxidation state would also cause an increase in pH of the fluids. The presence of unreplaced carbonate on both sides of the Essex pipe (e.g., Fig. 5), however, indicates that reaction with carbonate alone did not produce the high inferred solution pH's characteristic of the the western pyrrhotite-pyrite zone. Fluctuations in sulfur isotopic ratios over short distances in the pyrrhotite-magnetite-pyrite zone (Fig. 14a) are probably caused by minor fluctuations in fluid oxidation state (as suggested by fluctuations between pyrite, magnetite, and pyrrhotite stability in this zone; Eastman, 1980).

The model presented here hypothesizes that fluids were derived from a source below the central part of the Essex orebody, and not from the adjacent Darwin stock. Hence, the absence of mineralization and appreciable alteration in the Darwin stock is not mysterious--Pb-Zn skarn-forming fluids were not generated by the Darwin stock. The absence of Pb-Zn skarns to the E of the Darwin stock (Fig. 1) is related to the absence of granite porphyry bodies in that area. Further, the "distal" nature of Pb-Zn skarns (Einaudi et al., 1981) is re-affirmed, as the orebodies are adjacent to the Darwin stock, but extend outward from a deeper source, unexposed at present in the Essex pipe, but seen at the Defiance pipe. Finally, the relatively low ($<400^{\circ}C$) ore fluid temperatures can be reconciled with a magmatic source, given that (1) the most likely source lies at depth below the orebody, (2) the source was a high-F granite (Newberry, 1987) with a solidus temperature of about 550°C, and (3) the ore fluids cooled as they rose and moved outward.

Mechanism for ore deposition

Rye et al. (1974) ague that ore depositon at Darwin took place largely due to increase in pH under nearly isothermal conditions. The combined isotopic and sphalerite compositional systematics suggest that ore deposition was more complex, and especially that temperature decrease also played an important role. If increase in pH was the major cause of ore deposition, one would expect higher ore grades/tonnages on the W side of the Essex pipe than on the E side of the pipe (c.f., Fig. 15), as more drastic pH changes occur to the W. Such is apparently not the case, as shown by the historic mining record and by the distribution of stopes in the Essex area (Fig. 16). Isotopic, mineralogic, and sphalerite composition data suggest that pH actually <u>decreased</u> towards the top of the Essex pipe (Fig. 15), yet the most Ag- and Pb-rich ores are present in the upper parts of the pipe (Fig. 9). Changes in pH could not have been very great in the Defiance pipe, as only small changes in sphalerite composition (range of 3-5 mole % FeS; Fig. 13) and S-isotope ratios (Rye et al., 1974) are recorded--yet a large orebody is present. Further, sulfide precipitation by pH increase only operates for Cl-complexed metals. Under the low oxidation state, moderate pH (c.f., Fig. 15), and moderate temperature (300-400°C) conditions which the Darwin skarns experienced, the bulk of Cu and Zn transport by Cl complexes is likely, but an appreciable fraction of the Pb and Ag, and probably most of the Au were transported by bisulfide complexes (Wood et al., 1987). Oxidation state decrease causes precipitation of Cl-complexed metals, but increases solubility of bisulfide-complexed metals--hence, this mechanism also fails to solely explain sulfide deposition.

On the other hand, the bulk of ores--as recorded by the distribution of stopes--were deposited in a zone representing temperature decrease from 375°C to about 300°C (Fig. 16), representing the change from sulfides stable with garnet to sulfides associated with garnet destruction. Sulfides record a >125°C range in temperature of deposition from deep in the skarn pipe to the fringes of the pipe, with a lateral temperture gradient in excess of 1°C/meter (Fig. 16). Such a thermal gradient alone will cause an appreciable amount of sulfide deposition (Brimhall and Crerar, 1987).

Apparent absence of a lateral thermal gradient in the Defiance pipe (Fig. 13) is related to sampling restricted to the pipe core. Deposition of sulfides mostly by temperature decrease is consistant with the small changes in sulfur isotope ratios and sphalerite compositions seen in that pipe.

Comparison with other Pb-Zn skarns

Relative to other Pb-Zn skarns "proximal" to intrusions (Einaudi et al., 1981; Meinert, 1987; Megaw et al., 1988) the most outstanding features of the Darwin Pb-Zn skarns are the small proportion of pyroxene and the high Pb/Zn and Ag/Pb+Zn ratios. Indeed, the metal ratios for Darwin plot well within the range seen for sulfide mantos and far from typical skarn ores on the Pb-Zn-Ag plot of **Megaw et al.** (1988) and Cu-Pb-Zn plot of Yun and Einaudi (1982). The most obvious explanation for the low abundance of pyroxene is the abundance of aluminous calc-silicate rocks in the stratigraphy which caused high Al solution activities and stabilized garnet and idocrase. Such a contention might be supported by the late, highly aluminous garnets stable with sulfide and oxides (e.g., Fig. 7). Another high-garnet Pb-Zn skarn is the Mineral King deposit in central California (Einaudi et al., 1981), similarly hosted by an Al-rich stratigraphy.

The calc-silicate compositions are also unusual for a Pb-Zn skarn, with low-Fe,Mn pyroxenese characteristic. The closest match in pyroxene compositions are the Capote basin Zn-Cu skarns (Fig. 8), which predate and are not genetically related to the nearby Cananea Cu-rich breccia pipes (Meinert, 1982). High Mg contents in Pb-Zn skarn pyroxenes are considered indicative of proximity to the fluid source (e.g., Meinert, 1987), which is compatible with a granite porphyry body seen deep in the Defiance pipe. Lack of evolution to high Fe-Mn contents is probably related to the apparent instability of pyroxene in the skarn.

The unusual--for a skarn--metal ratios at Darwin (Einaudi et al., 1981) may result from both stratigraphic and thermal effects. The relatively small amount of carbonate rock in the stratigraphy (Figs. 2, 5) may have caused smaller than usual pH increase during skarn formation, yielding smaller than usual amounts of precipitation by Cl-complexed metals (Cu,Zn) relative to HS-complexed metals (Pb,Ag). Burt (1972) has noted a strong correlation between high-Fe pyroxenes and high Zn abundance in Pb-Zn skarns; the absence of high-Fe pyroxenes at Darwin may have caused less-than-usual Zn deposition, yielding abnormally high Pb/Zn ratios. Finally, the strong lateral thermal gradient present (Fig.16) may have caused more effecient than usual precipitaiton of the more soluble Pb and Ag closer to the skarn body (commonly within the skarn), resulting in higher levels of these latter elements in the skarn.

At first glace, the Darwin deposit might be described as having a much greater thermal gradient than observed in other Pb-Zn skarns: <50°C for Providencia, Mexico (Sawkins, 1964) and 23°C/km for Groundhog, New Mexico (Meinert, 1987) relative to the 100°C/100 m lateral gradient for Darwin. Based on data for the above studies, Megaw et al., 1988, concluded that fluid cooling is not a major control on mineralization in Mexican Pb-Zn skarn-manto deposits. The thermal gradients for both the above studies, however, are gradients <u>along the fluid conduit</u>, not perpendicular to the fluid conduit. Meinert (1987) showed a dike-to-marble thermal gradient of 35-50°C/5-20 meters; although a higher gradient than that seen at Darwin, a lower absolute decrease in temperature. Two conclusions are probably justified: (1) absolute decrease in temperature is probably common in Pb-Zn skarns (2) the geometry of isotherms varies considerably. The latter effect is not only important in developing chimney vs. manto morphology (Megaw etal., 1988), but developing Pb-Zn skarn morphology and zonation patterns. Hence, the idealized Pb-Zn skarn zonation model of Meinert (1987) is not only restricted in applicability to those Pb-Zn skarns with similar marble-dominated stratigraphies, but also to those with similar dike-related isotherm patterns.

CONCLUSIONS

The Darwin deposits, exhibit some, but not all, the characteristics of "typical" Pb-Zn skarns and illustrate the dangers inherent in promulgating ore deposit models. Variations in stratigraphy and isotherm patterns may cause major variations in skarn appearance and metallogeny and result in the Darwin skarns being quite atypical of Pb-Zn skarns. The presence of multiple plutonic/hydrothermal--perhaps common in many ore districts--causes multiple zonation patterns, as in the zonation of most minerals around the skarn pipes, but the pyrite/pyrrhotite zonation around the pre-Pb-Zn skarn Darwin stock. Because sulfur isotope fractionation factors are relatively insensitive to temperature in the 300-400^{O}C range, metal deposition at Darwin has been treated as a simple, essentially isothermal process. In detail the process was complex, probably took place over a temperature decrease of >125^{O}C, and probably involved complex (Fig. 15) but inter-related changes in solution pH, oxidation state, and major element chemistry.

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