ZONED SIDERITE PORPHYROBLASTS FROM THE ESPLANADE RANGE AND NORTHERN DOGTOOTH MOUNTAINS, BRITISH COLUMBIA

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ABSTRACT

Siderite porphyroblasts from Precambrian phyllites (greenschist facies) of the Esplanade Range and Northern Dogtooth Mountains, British Columbia (51°31′N, 117°27′W) show concentric optical zoning and electron microprobe study indicates strong chemical zoning. Manganese content generally decreased during crystal growth and most of the manganese zoning pattern can be interpreted by a simple depletion model during crystal growth.

INTRODUCTION

Siderite occurs as porphyroblasts in phyllites from the Horsethief Creek Group (Hadrynian) in the Esplanade Range and Northern Dogtooth Mountains, British Columbia (51°31′N, 117°27′W). The siderite is most prominent in the biotite-chloritoid zone of metamorphism and is replaced by other ferromagnesian minerals in the garnet zone.

The size of the siderite prophyroblasts averages near 3 to 4 mm in diameter and they have elliptical to circular outlines in thin section (Fig. 1). The siderites are commonly associated with quartz, phengites, and a complex accessory assemblage of calcite, rutile, pyrite, pyrrhotite, chalcopyrite, arsenopyrite, and cobaltite. Elsewhere the siderites occur with quartz-phengite-chloritoid-paragonite assemblages. Quartz and phengite commonly occur as inclusions in the siderite prophyroblasts and define an internal schistosity (S_1). This schistosity is associated with the earliest fold episode (F_1) in the Esplanade Range (De Vries *et al.*, 1971). Siderites are deformed by a later deformation (F_2). Biotite and chloritoid porphyroblasts, as well as siderite, have crystallized post-F_1 and pre-F_2 and, by implication, siderite has grown during greenschist facies metamorphism.

One of the most striking features of the siderite porphyroblasts is the development of concentric optical zoning (Fig. 1). The zoning consists of an *inner core*, making up about one-half the diameter of the crystal, followed outward by a *colorless zone*, generally about 0.3 mm wide, and an *outer margin*. The *inner core* and *outer margin* contain numerous fine grained inclusions but the *colorless zone* is comparatively inclusion-free.

The quartz inclusions are elongate and well-rounded and are generally of slightly smaller diameter than the groundmass quartz, implying that
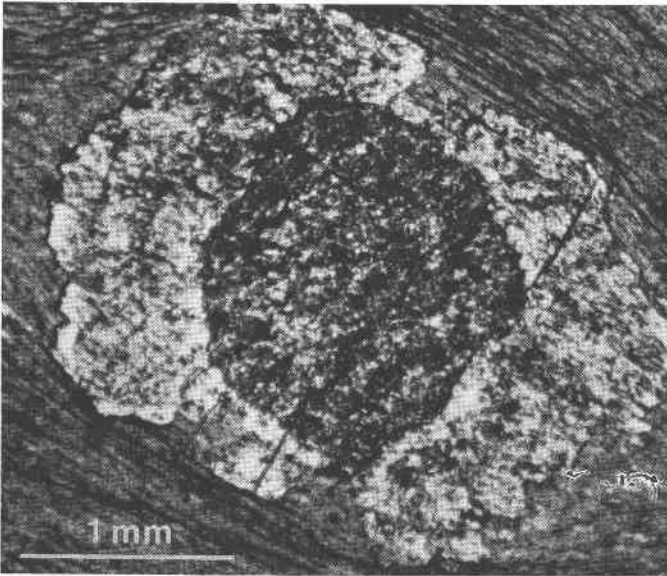
Fig. 1. Microphotograph of optically zoned siderite porphyroblast. The central darker portion of the crystal makes up the *inner core*. This is succeeded outward by the *colorless zone* containing relatively few inclusions and the *outer margin*.

grain growth of quartz took place during and continued after crystallization of the siderite porphyroblasts.

In the present paper we describe the compositional zoning of siderite porphyroblasts from phyllite containing the assemblage quartz-phengite-siderite $\pm$ calcite-rutile-pyrite-chalcopyrite-pyrrhotite-arsenopyrite-cobaltite.

Electron Microprobe Procedures

The instrumental operating conditions were: accelerating voltage 15 kV, emission current 200 μA, beam diameter about 1 μm, beam current 0.05 μA, integration times about 100 sec. (beam current integration was used to terminate counting).

The following elements were analyzed simultaneously: Fe, Mn, and Mg; Fe, Ca, and Mg; Ca, Mn, and Mg (with Fe by solid state detector). A great deal of care was used in the selection of spot analyses because of the large number of inclusions. Silicon was monitored simultaneously on an oscilloscope display of output from a Kevex solid state detector and Nuclear Data multichannel analyzer. When a SiKα peak was detected the spot analysis was rejected.

Standards used were Elba hematite (Fe), calcite (Ca), forsterite (Mg), and rhodonite (Mn). Data were corrected for background and drift and were reduced according to procedures outlined by Bence and Albee (1968). Fe, Ca, Mg, and Mn were analyzed as oxides and were converted to equivalent carbonates (Macqueen and Ghent, 1970). Summations of the carbonates usually fell in the range 98 to 102 percent. Precision of the analyses are indicated in Figures 2 and 3. No analyzed Fe-Mg carbonate was available for comparison
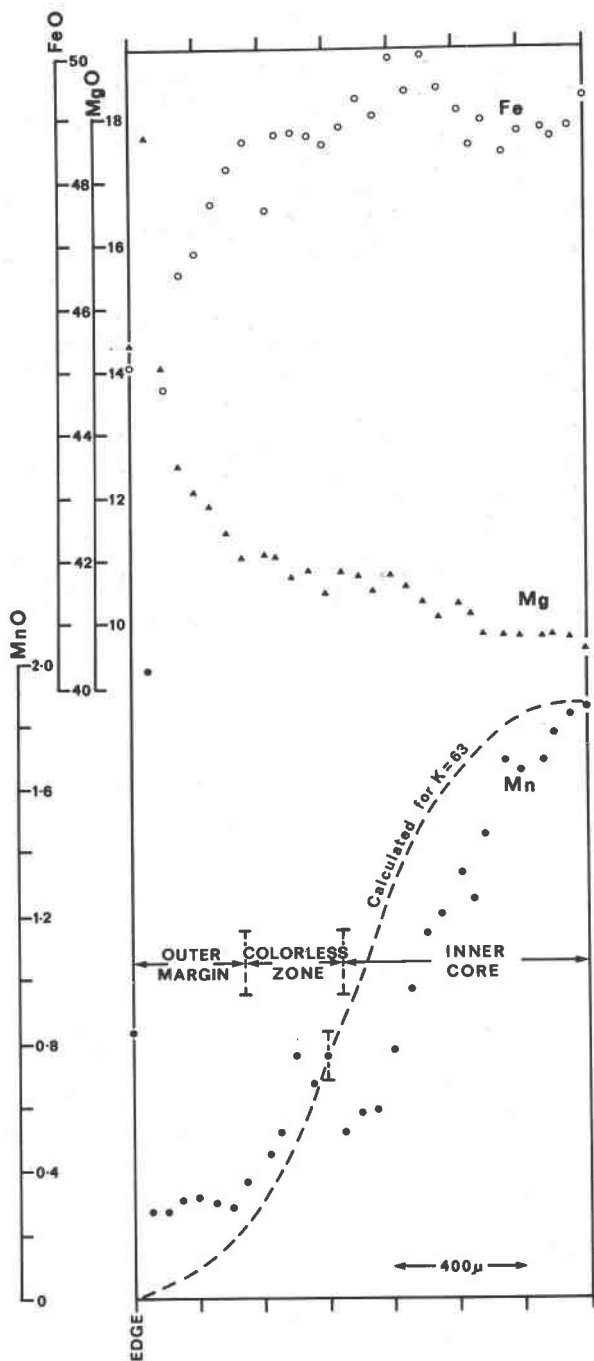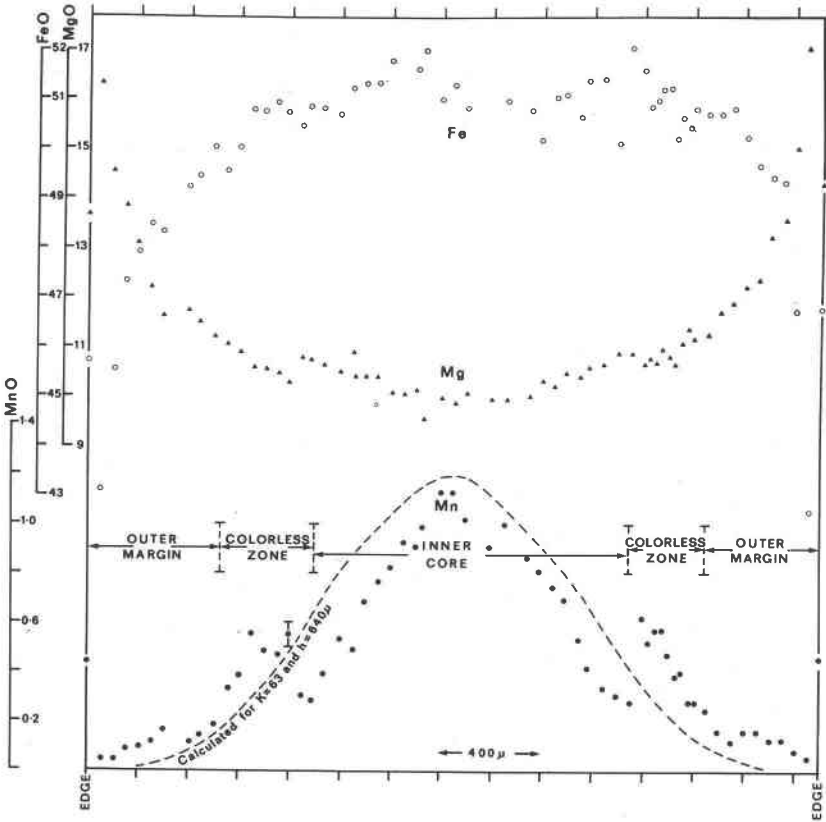
Fig. 3. Fe, Mg, and Mn profiles across siderite crystal in which section did not pass through exact center of crystal. See text for explanation. Note increase in Mn at extreme edges of crystal.

but the major elements are considered accurate to better than 2 percent of the amount present and the minor elements to better than 10 percent of the amount present.

ZONING PATTERNS

Profiles across two grains are presented in Figures 2 and 3. The most noteworthy features of the profiles are: 1) a high concentration of Mn in

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Fig. 2. Fe, Mg and Mn profiles across siderite porphyroblast. This is considered to pass through exact center of crystal. Dashed line on Mn profile is calculated profile for K = 63 and length of vertical bar on Mn profile indicates 3σ (three times standard deviation of total counts per spot) for precision of Mn analyses. Note increase in Mn at extreme edge of crystal.

the *inner core* followed by a steady outward decrease in Mn content to the margin of the *colorless zone*. An increase in Mn content in the *colorless zone* is followed by an outward decrease and then a small increase in Mn at the edge of the *outer margin*; 2) Fe and Mg contents vary sympathetically in the profiles with Fe decreasing toward the margins of grains. No break in Fe-Mg zoning is observed in the *colorless zone*, but, at the edge of a crystal Fe typically shows a sharp increase and Mg a sharp decrease; 3) Ca shows an irregular profile but tends to be higher in the cores than at the margins. This pattern of zoning could be reproduced in all seven of the optically zoned grains which were investigated.

It is of interest that the patterns of Mn zoning described above, that is, a general decrease in Mn content during crystal growth has been observed by other workers in almandine-rich garnets (*e.g.*, Hollister [1966], Atherton [1968], Dudley [1969]). Hollister (1966) and Atherton (1968) have interpreted this Mn zoning by a depletion model during crystal growth following the theoretical reasoning outlined by Rayleigh (1902), Pfann (1952), and McIntire (1963).

All depletion models are of the form $C = kC_o(1-F)^{k-1}$ where C is the concentration of a minor element in any particular zone, k is the fractionation factor between the porphyroblast and the solute, C_o is the initial concentration of the element in the solute, and F is the weight fraction crystallized up to and including the zone.

The profile of Figure 2 is considered to pass through the exact center of the siderite porphyroblast where $C = 1.88$ wt. percent and $F = 0$. X-ray fluorescence analysis of the bulk sample gives 0.03 wt. percent MnO, whence $k \simeq 63$.

Using this value of k and taking any point on the smooth profile between the center and the inner edge of the *colorless zone* of this profile, the depletion expression may then be solved for F, the fraction crystallized, whence the radius of the sphere from which Mn is diffusing into the porphyroblast may be calculated. From the profile in Figure 2, a radius of diffusion (R) of approximately 3.3 mm is obtained from $0.52 = 63$ (0.03) $(1 - 750^3/R^3)^{62}$ (where the MnO content at a point $750\,\mu$ from the center of the porphyroblast was measured as 0.52 wt. percent). This expression has not been corrected for the difference in density between the siderite and the average matrix and assumes a constant k during growth.

To check this radius R, and the assumption that it is similar for all porphyroblasts, h^3/R^3 may be substituted for F in the depletion expression above. (h, the height of the section above the true porphyroblast

TABLE 1. COMPARISON OF ACTUAL AND ESTIMATED MnO CONTENT
OF APPARENT CENTERS OF PORPHYROBLASTS

Sample	Apparent radius (μ) of porphyroblast	Inner radius of colorless zone (μ)	Calculated height (h) of section above true center (μ)	Calculated MnO content of apparent center (wt %)	Observed MnO content of apparent center (wt %)
366/1 grain #4	1550	325	890	0.57	0.48
366 grain #2	1450	550	640	1.20	1.14
366 grain #4	1325	618	835	0.66	0.77

center can be estimated from simple trigonometrical considerations by assuming that the *colorless zone* formed after the same percentage crystallization in all porphyroblasts). This procedure yields values of C for the concentration of MnO at the apparent centers of porphyroblasts sectioned at a distance h from their exact centers. The results, presented below in Table 1, suggest that the method is correct and that a spherical porphyroblast is a reasonable assumption.

The calculated Mn profiles, using the depletion expression cited above, presented in Figures 2 and 3, were made assuming $k = 63$. The profile in Figure 3 was calculated assuming a radius of diffusion, R, of 3.3 mm (obtained from profile 2) and a section height above the exact center of 640 μ. It can be seen that the calculated profiles fit the observed profiles quite closely until the *colorless zone* is reached.

INTERPRETATION

Since the theoretical profiles from the centers to the *colorless zone* agree reasonably well with those actually observed, the implication is that as each infinitesimally thin layer was precipitated it was in equilibrium with the matrix whereas the layers were not in equilibrium with each other.

The change in zoning pattern at the *colorless zone* has several possible interpretations. Among these are: 1) a change in k due to a change in temperature during growth; 2) breakdown of another mineral during growth to release more Mn in the system; 3) change in rate of growth of crystals due to factors other than changing temperature, *e.g.*, changes in fluid composition.

The change in zoning pattern is not likely to be due to an increase in temperature because k usually decreases with increasing temperature and this would cause the profile to shift in the opposite direction. A decrease in temperature is, however, a possibility.

There is no evidence for release of Mn due to breakdown of another mineral. Phengite (0.3 percent MnO) is the only other major constituent carrying appreciable MnO. Exchange reactions between siderite and phengite are likely to have affected the Mn zoning pattern but there is no reason to believe that k changed because of a breakdown reaction involving phengite.

The explanation favored by the authors is than Mn depletion occurred along an equilibrium profile until the time at which the *colorless zone* started to form. At this point a decrease in temperature or a change in fluid composition caused a change in growth rate of the siderite. New equilibrium was established causing an initial increase in MnO content and then a steady depletion. The rise in Mn (and Fe) near the outer edge of the crystal could represent slight changes in temperature or disequilibrium crystallization during the waning stages of porphyroblast growth.

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