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# Zinc-manganese carbonates from Broken Hill, New South Wales

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ABSTRACT. Specimens of honey-brown to pinkish-brown globular carbonates encrusting concretionary goethite-coronadite from the oxidized zone at Broken Hill, New South Wales, have compositions in the rhodochrosite-smithsonite series. This may be the first extensive natural occurrence of this solid-solution series. Growth of the carbonates occurred in zones which have near uniform composition. The ratio $MnCO_3/(MnCO_3+ZnCO_3)$ for each zone bears a linear relationship to the measured $d$ spacing for the $10\bar{1}4$ X-ray reflections. Because cerussite is the only other mineral associated with the Zn-Mn carbonates and because of an absence of detailed locality information, the paragenetic significance of these minerals cannot be determined. The solutions depositing them may have been derived from the near-surface equivalents of the Zinc Lode horizons.

KEYWORDS: carbonates, rhodochrosite, smithsonite, Broken Hill, New South Wales, Australia.

THE carbonate mineralogy of the extensive oxidized zone at Broken Hill is one of that orebody's least studied and hence most poorly understood features. As mining has removed all but a vestige of the original oxidized zone, investigation of the wide range of carbonate minerals is restricted to specimens in museum collections.

In an attempt to document this diversity, specimens in the Museum of Victoria collection were examined by routine X-ray diffraction and electron microprobe techniques. The study concentrated on encrusting and botryoidal forms (e.g. Birch, 1983) rather than on the more abundant, well-crystallized species, such as cerussite and smithsonite.

One unusual variety of encrusting carbonate occurs as honey-brown, pinkish-brown, and yellowish-brown globules or botryoidal coatings on banded concretionary goethite and coronadite (figs. 1 and 2). These have all been labelled as rhodochrosite in museum collections, based on early descriptions of fawn-coloured, mammillated and spheroidal forms under that name by Smith (1926). However, X-ray diffraction tests on several specimens showed departure from the expected rhodochrosite pattern.

Seven individual specimens, five from the Museum of Victoria and two from the Australian Museum, were investigated. Six consisted of individual globules and intergrown hemispheres up to 2 cm in diameter on cavernous goethite/coronadite (fig. 1), while the seventh was a continuous encrustation (fig. 2). The surfaces of all specimens had a sparkling appearance due to minute intergrown rhombic terminations. On three specimens, a very thin, near colourless to pale pink or pale yellow layer formed the outer surface. Broken open, the globules and crusts showed concentric growth shells, some of which were separated by a thin layer of pale carbonate. Others were distinguished by either a sudden or gradual colour change. Occasionally, concentric zones were separated by narrow gaps.

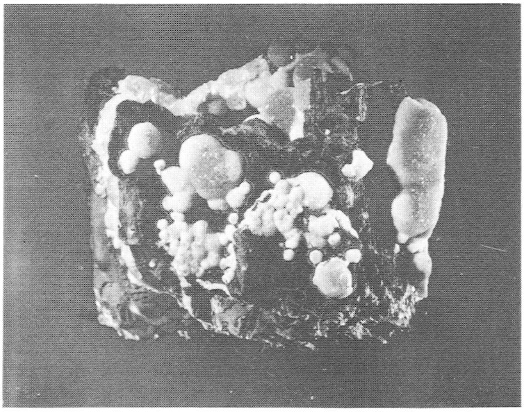

FIG. 1. Globular, yellow to honey-brown Zn-Mn carbonate on coronadite/goethite matrix. Specimen is 7 cm across (Museum of Victoria, M2439).

In thin section, the concentric zones often showed a fibrous radiating texture giving rise to undulose extinction. However, the degree of coarseness between each zone was variable. Zones ranged

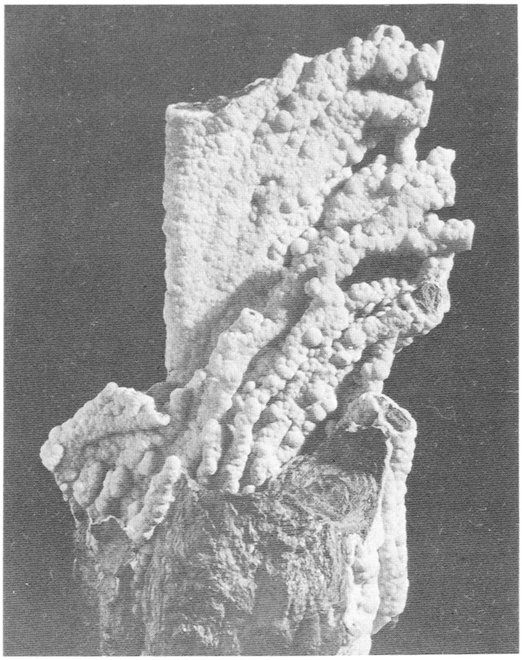

FIG. 2. Encrusting, fawn Zn–Mn carbonate on coronadite/goethite. Specimen is 12 cm high (Museum of Victoria, M27294).

from aggregates of anhedral grains within each of which the structure was finely fibrous, to zones made up of anhedral grains which extinguished uniformly. Generally, the outermost layer showed the most optically clear crystallinity. Growth stages were recognizable by relatively sudden changes in texture and by very thin concentric zones of opaque earthy carbonate.

The only other associated mineral was cerussite, on three specimens. In all examples, the encrusting carbonate was deposited directly on to the geothite/coronadite matrix.

*X-ray diffraction.* Where possible, portions of different zones on all samples were carefully separated for X-ray powder diffraction analysis. Using Ni-filtered Cu-K$\alpha$ radiation, smear mounts were run at a scanning rate of 0.25°/minute, a chart speed of 2 cm/minute and with synthetic $CaCO_3$ as an internal standard. The separation of the $10\bar{1}4$ reflections for the sample and the standard were measured directly on between 3 and 8 chart runs per sample. The position of the $10\bar{1}4$ reflection for $CaCO_3$ was taken as 3.035 Å (JCPDS standard 5-586). These results are shown in Table I.

In general, the $10\bar{1}4$ reflections for the natural carbonates were sharp. Where otherwise, broadening or doublets could be attributed to a range in composition within the one zone or to incomplete

Table I. Description and summary of composition and X-ray diffraction data for zinc-manganese carbonates (*data plotted in fig. 4).

| Sample No. | Zone Description | Width (mm) | $d(10\bar{1}4)$ (Å) | $MnCO_3/(MnCO_3 + ZnCO_3)$ (average) |
|---|---|---|---|---|
| M2439 | * Inner, honey brown fibrous-granular core with included coronadite | 1-2 | 2.830 | 0.70 |
| | * Outer, yellow brown granular rim, grains oriented radially | 0.7 | 2.840 | 0.80 |
| M2441 | * whole sample, slight change from fibrous core to granular rim | 2 | 2.850 | 0.89 |
| M5370 | * coarse granular outer zone | 0.8-1 | 2.844 | 0.83 |
| | * core varying from coarse granular to fibrous | 1.6-1.9 | 2.831 | 0.69 |
| M27294 | * finely fibrous greyish brown inner zone | 0.9 | 2.807 | 0.47 |
| | soft white zone | 0.2 | - | 0.62 |
| | finely fibrous yellowish brown outer zone. (variable composition - see Fig. 5) | 0.3-0.5 | 2.814 | 0.39-0.70 |
| | darker fawn crystalline rim (Ca-rich) | 0.1 | 2.858 | 0.87 |
| D27980 | * finely fibrous pinkish brown inner zone | 1.1 | 2.818 | 0.56 |
| | * granular white - pale pink outer rim | 0.15 | 2.848 | 0.86 |
| D34814 | * white - pale pink crystalline rim (outermost colourless). | 0.2 | 2.850 | 0.87 |
| | * pinkish brown, finely fibrous outer zone of core. | 1 | 2.823 | 0.60 |
| | white layer between inner and outer core | 0.1 | - | 0.63 |
| | * pinkish brown, finely fibrous inner zone of core | 0.8 | 2.832 | 0.69 |

separation of two adjacent zones of differing composition.

*Electron microprobe analysis.* In order to relate variation in the 10$\bar{1}$4 spacing to composition, fragments of all X-rayed zones, or the complete globules, were analysed by electron microprobe, with the beam defocused to around 30-40 $\mu$m diameter at 15 kV and with specimen currents of about 0.02 $\mu$A. Metals (Fe, Cu, Zn, Mn), periclase (Mg), and wollastonite (Ca) were used as standards.

Spot analyses in traverses across the entire zonal sequence in selected samples were carried out as well as random analyses on individual zones. The results showed that the carbonates were almost entirely confined to the smithsonite-rhodochrosite series, with $MnCO_3/(MnCO_3+ZnCO_3)$ ranging from 0.9 to 0.4. This is possibly the first record of extensive solid solution in the Zn-Mn carbonate series occurring naturally. The compositional zoning patterns, for $MnCO_3/(MnCO_3+ZnCO_3)$ and $PbCO_3$, are shown in fig. 3.

The data also indicate that: (*a*) compositions are quite uniform within most zones; (*b*) the outermost zone is generally closer to the rhodochrosite end

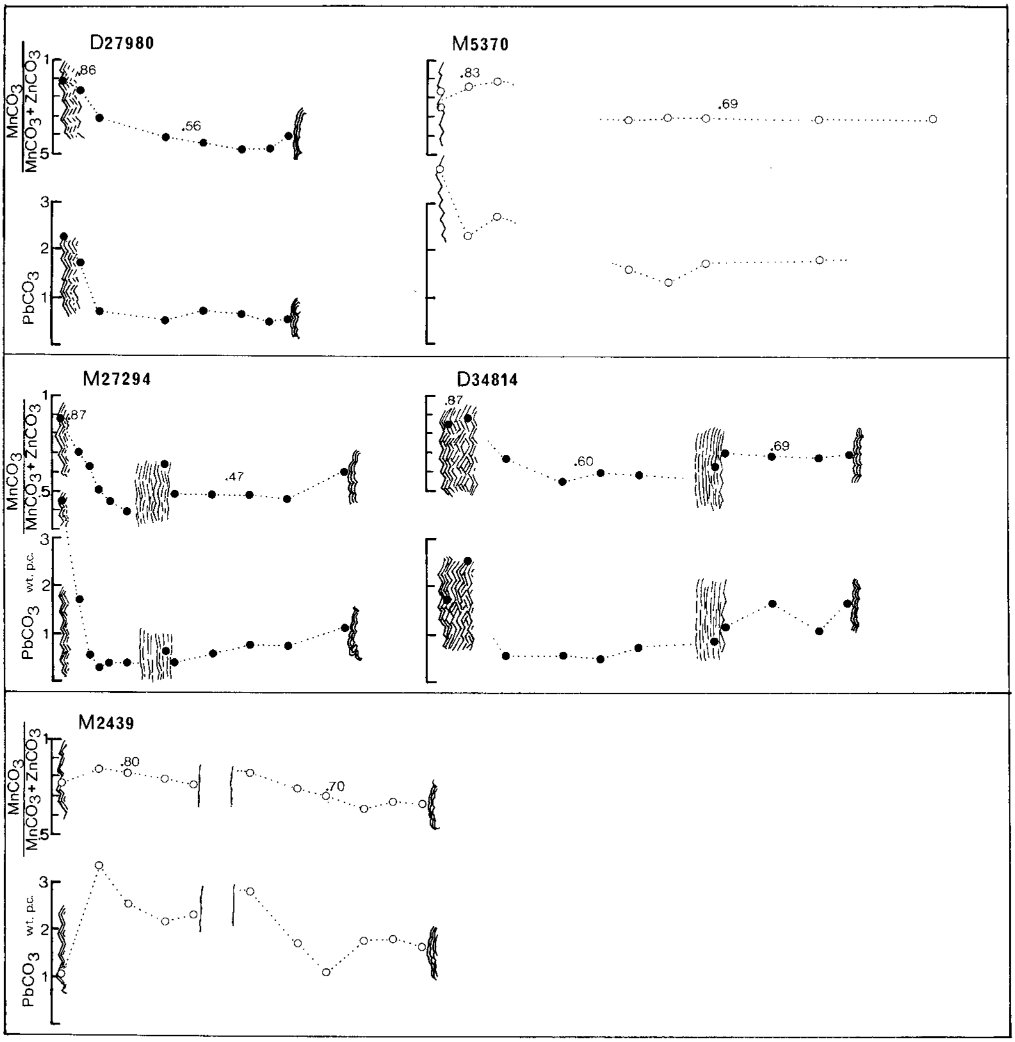

FIG. 3. Simplified diagram showing compositional zonation ($MnCO_3/(MnCO_3+ZnCO_3)$ and wt. % $PbCO_3$) across five specimens. Zig-zag areas are outer crystalline rims; inner contact with matrix marked by concentric bands. Gaps and opaque or soft zones also shown. Average value of ratio indicated for each zone. Note overall similarity between profiles for M5370 and M2439. All profiles drawn to same scale—that for D27980 is 1.5 mm across.

member; (*c*) Pb contents tend to be highest in zones where $MnCO_3/(MnCO_3+ZnCO_3)$ is greatest (fig. 3); (*d*) zones showing finely fibrous textures have lower $MnCO_3/(MnCO_3+ZnCO_3)$ ratios than coarser grained granular zones.

*Discussion.* A plot of $10\bar{1}4$ spacings (Table I) versus the average value of $MnCO_3/(MnCO_3+ZnCO_3)$ for each zone reveals a linear relationship (fig. 4) extending for over half the possible solid-solution series. The points lie close to the straight line joining smithsonite and rhodochrosite end members. The slightly greater $10\bar{1}4$ spacings observed in the natural minerals than in the pure $ZuCO_3$-$MnCO_3$ series is the result of the effects of larger cations such as Pb and Ca. A similar effect is shown in the plot of $ZnCO_3$ versus $MnCO_3$ for all analyses (fig. 5). The displacement from the pure Zn-Mn carbonate line is greatest for Mn-rich carbonates, where ease of substitution of Pb and Ca appears to be enhanced.

The linearity of the $10\bar{1}4$ spacing-composition relationship suggests that other properties such as refractive indices and density would also vary linearly with composition.

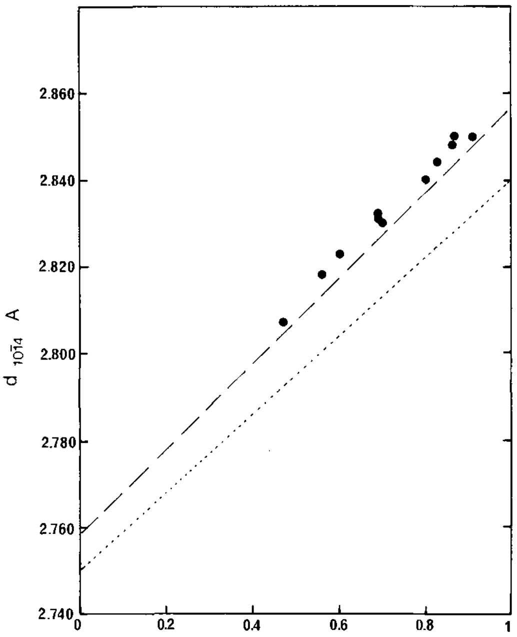

FIG. 4. Plot of average $MnCO_3/(MnCO_3+ZnCO_3)$ versus $d(10\bar{1}4)$ for zones described in Table I. Dashed line joins rhodochrosite and smithsonite end members determined by same methods as samples (see text). Dotted line joins end members based on JCPDS data.

Naturally occurring, nearly pure carbonates in the smithsonite-rhodochrosite series have not, to the author's knowledge, been reported previously. Nor have phase relations in the binary system been investigated experimentally (Goldsmith, 1983). However, from the small difference in ionic radii between zinc and manganese (Mn = 0.80 Å; Zn = 0.72 Å: $\Delta = 0.08$ Å) it is likely that complete miscibility occurs, since cationic size is the main factor influencing the degree of isomorphic solid solution in the *R*3*c* carbonates (Reeder, 1983). The limited preference shown by Pb ($r = 1.2$ Å) and Ca ($r = 1.0$ Å) for the more Mn-rich compositions can be explained in terms of their ionic radii being closer to Mn than the smaller Zn cation. Since it would be easier for small ions such as Mg and Fe to substitute for larger ions in the rhombohedral carbonate structure than the reverse, the near-absence of Mg and Fe in the Broken Hill Mn/Zn carbonates is attributable to a lack of these elements in the carbonate-forming solutions.

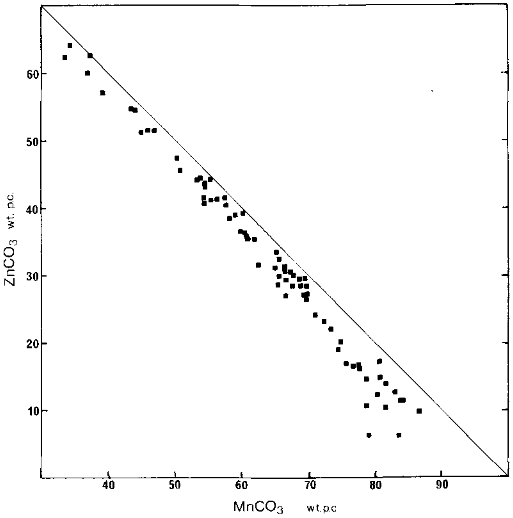

FIG. 5. Plot of $ZnCO_3$ versus $MnCO_3$ for all microprobe analyses obtained in the study. Note greater divergence from 1 : 1 line (for pure stoichiometric Mn-Zn carbonates) at Mn-rich end, due to enhanced substitution of Ca and Pb.

The Mn/Zn carbonates described here appear to have come from a restricted region of the oxidized zone, in the vicinity of the Central Mine. They are isolated from other carbonates in the zone, with the exception of cerussite, so their position in the overall paragenetic sequence is difficult to determine.

The rarity of this solid-solution series must be attributed to the scarcity of natural systems in which only Mn and Zn are available for carbonate formation. Both elements are in plentiful supply in the Broken Hill primary ore. So too are Pb, Fe, Cu, and Ca—their absence in significant quantities from the low-temperature solutions forming the Mn/Zn carbonates provides yet another example of the complexities of this unique orebody.

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