

Rhodochrosite from Islay, Argyllshire and Dalroy, Inverness-shire, Scotland

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Abstract

Rhodochrosite has been discovered as a minor component of two manganese deposits in Scotland. At Islay it occurs as coatings and veinlets on and within hollandite–pyrolusite–hematite–goethite mineralisation. Two foram microfossils were found within the carbonate which is considered to have formed from the interaction of organic-rich groundwater and seawater. The Dalroy rhodochrosite has the form of stromatactis-like cavity infill structures and veinlets in a mineralogically complex manganese–iron ore in which braunite, bustamite, manganian ilmenite and pyrophanite have been identified. Intergrowths of rhodochrosite and native copper grains occur in a calcite matrix within the infill structures. These intergrowths are typically one micrometre across, but achieve diameters of up to 50 μm . The genesis of the Dalroy rhodochrosite is more problematical, although a hydrothermal source is most likely.

KEYWORDS: rhodochrosite, native copper, Islay, Dalroy, Scotland

Introduction

RHODOCHROSITE is commonly found as a primary component in hydrothermal vein deposits and in both metamorphosed and unaltered sedimentary ores. It is also known to occur in lacustrine and marine manganese nodules and crusts as a diagenetic alteration product (see Roy, 1981, pp. 54, 56, 160; Table XVIII for a thorough literature review). Previously unrecorded in Scotland, this paper describes the rhodochrosite discovered as a minor component in two distinct manganese deposits.

Islay

Occurrence. Veins, coatings and discrete masses composed of mixed iron and manganese oxides occur on the south-west of the island within the Jura Quartzite (Dalradian Supergroup) which is of Precambrian–Cambrian age. The mineralisation is located below an ancient fort known as Dun Athad, on the western side of a narrow headland, part of the Mull of Oa peninsula [NR 283 406]. The iron oxides are composed of hematite and goethite in variable amounts, while hollandite is the principal manganese mineral together with pyrolusite and minor groutite (Nicholson, unpubl. data).

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Reflected light microscopy. The rhodochrosite was discovered in a polished section of a single specimen collected from the landward end of the headland. The carbonate occurs as coatings on hollandite and as veinlets cutting hollandite and hematite (Fig. 1). It was in one such coating that two microfossils were found. These were identified as forams (Mike Keen, pers. comm.), but owing to the two-dimensional appearance of the fossils in the section, no precise identification could be made.

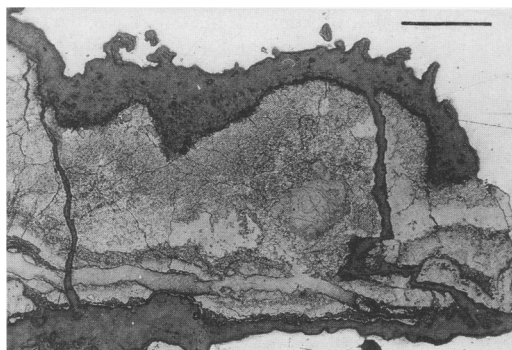


FIG. 1. Photomicrograph of Islay rhodochrosite coatings and veinlets (dark grey) on hollandite (light grey, speckled appearance) and hematite (light grey, more solid appearance, better polished). Bar = 0.5 mm.

TABLE 1: Mean electron microprobe EDS analyses of rhodochrosite (Rc) and manganoo calcite (Mn-Ct) from Islay and Dalroy.

	Islay		Dalroy	
	Rc n=11	Mn-Ct n=6	Rc n=15*	Mn-Ct n=8
wt %				
MnO	52.1 (4.7-54.4)	11.4 (9.9-12.3)	51.7 (46.4-56.2)	7.3 (4.8-8.6)
CaO	5.0 (2.6-7.8)	39.9 (39.0-40.6)	4.6 (1.9-9.8)	41.9 (38.7-44.1)
MgO	3.6 (2.8-5.2)	4.3 (3.6-4.9)	<0.5 (<0.5-1.6)	<0.5 (<0.5)
FeO	<0.5 (0.5)	<0.5 (<0.5)	<0.5 (<0.5-1.7)	<0.5 (<0.5)

*two analyses contain 2.5%, 2.8% CuO; Zn<0.5% in all analyses

Chemical composition. Electron microprobe studies identified the presence of rhodochrosite with associated manganoo calcite and calcite. Rhodochrosite rarely occurs as pure MnCO_3 as Fe(II), Zn(II), Ca(II) and Mg(II) ions readily substitute for Mn(II). As shown by the analyses (Table 1), Ca and Mg are present in the Islay samples, but Fe and Zn were not detected. These yield a formula of $(\text{Mn}_{0.8}\text{Ca}_{0.1}\text{Mg}_{0.1})\text{CO}_3$ for the rhodochrosite while that of the manganoo calcite calculates to $(\text{Ca}_{0.7}\text{Mn}_{0.2}\text{Mg}_{0.1})\text{CO}_3$. Insufficient material was available for XRD analysis.

Genesis. It is clear from ore microscopy that the carbonate coatings and veinlets post-date the manganese and iron oxides. This is unusual since when manganese oxides and rhodochrosite occur together, it is the manganese oxides which usually form after oxidation of rhodochrosite. Although Mn(III) and Mn(IV) oxides are invariably very stable in the surficial environment, they can be reduced to Mn(II) ions, and hence taken into solution, by reaction with organic acids (Baker, 1973). It is suggested that solutions rich in such acids, derived from the overlying organic-rich peat horizon, coated and penetrated the oxides along microfractures. These reacted with the manganese oxides to produce a surficial aqueous film of Mn(II) ions. Mixing of this film with seawater caused the carbonates to precipitate. This precipitation reaction is a consequence of the reduction in the ionic strength of the seawater on mixing with freshwater, as demonstrated by a consideration of the Debye-Huckel equation. This relates activity and ionic strength and at its simplest has the form

$$-\log \gamma_i = AZ_i^2 \sqrt{I}$$

where γ_i is the activity coefficient of species i , A is a constant characteristic of the solvent at a given temperature and pressure, Z_i is the ionic charge and

I is the ionic strength of the solution. The activity coefficient enables concentration and activity to be equated according to the expression

$$[i] = a_i/\gamma_i$$

where a_i is the activity of species i . Thus from these equations it is clear that if I is reduced then γ increases and hence the concentration of species i in solution decreases; i.e. when seawater is diluted, the solubility of calcium carbonate decreases.

After reduction of the manganese oxides by organic acids and the precipitation of the calcium carbonate, rhodochrosite was formed by the mechanism described by McBride (1979). In this, Mn(II) ions were initially chemisorbed onto carbonate surfaces. As the concentration of Mn(II) ions would have been locally greater than the amount of calcium carbonate present, the surface sites soon became saturated with Mn(II), following which rhodochrosite itself began to nucleate at the calcite surface. This nucleation was then followed by the slow precipitation of rhodochrosite as a discrete phase.

Support for such a genesis is provided by the chemistry of the carbonates. As stated, these contain small but significant quantities of Mg, a composition which is characteristic of carbonates precipitated from seawater (Callender and Bowser, 1976). In addition, similar (although rare) carbonate coatings were found on specimens collected from more seaward sites, and these coatings were composed only of calcite. This is precisely what would be expected from the above mechanism. These sample sites were well away from the peat horizon and therefore from the associated organic-rich solutions; thus no Mn(II) ions would be available for the formation of rhodochrosite, and hence only calcite was produced.

Dalroy

Occurrence. Manganese mineralisation at Dalroy was discovered earlier this century by Wallace (1919). It was described as occurring within ancient topographic depressions in the Dalradian granulite basement, being overlain by Middle Old Red Sandstone conglomerates and sandstones. Mining activity in the 1920s has left small dumps of the manganese and lesser iron ore [NH 766 448]. These now represent the only available material for examination since the discovery outcrop was excavated during mining. The deposit as a whole is mineralogically complex, and identification of many phases has yet to be achieved. However, the manganese ore is known to be composed of a mixture of oxides and silicates. XRD analyses have indicated the presence of braunite and bustamite while microprobe work has demonstrated that manganous ilmenite and pyrophanite are also present. Studies to confirm these and other tentative identifications are underway. It is in this complex ore that the rhodochrosite was discovered.

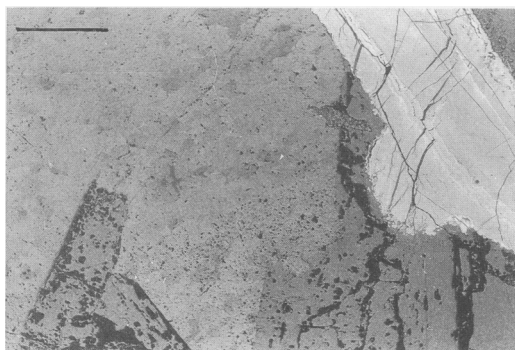


FIG. 2. Photomicrograph of polished section across a typical cavity-infill structure in Dalroy samples. Baryte laths (dark grey) and rhodochrosite are cut by (?) jacobsonite (light grey). Bar = 0.5 mm.

The carbonate occurs within cavity-infill structures which resemble stromatolites in many cases (cf. Bathurst, 1982). The infilling minerals are principally either calcite or rhodochrosite; occasionally both carbonates are present. The calcite displays a banded texture in some instances, as does the rhodochrosite, although this is rare. Baryte laths are also obvious in hand specimen. These cavity-like structures are surrounded (?supported) by broken and complete bands of colloform manganese oxides and silicates.

Reflected light microscopy. Under the microscope

baryte laths are seen to invariably line the cavity (Fig. 2). These laths and the carbonate are cut by veinlets of an unidentified iron-manganese oxide (?jacobsonite), which itself is often broken by the carbonates. All three phases also cut the fine-grained manganese oxide/silicate groundmass as irregular veinlets. Grains of native copper were observed within the carbonates of the cavity structures. These grains are typically one micrometre across, but examples up to 50 μm in diameter do occur. The grains display the usual optical properties of native copper and show an intimate association with rhodochrosite. Instances where both minerals include one another were observed; the combined rhodochrosite-copper grain is invariably included within a calcite matrix. No calcite-copper grains were found.

Chemical composition. The presence of manganous calcite in addition to rhodochrosite is demonstrated by the microprobe analyses in Table 1. Ca is the principal ion substituting for Mn in rhodochrosite, the levels of Fe, Zn and Mg being generally below the limit of detection. These analyses calculate to a formula of $(\text{Mn}_{0.9}\text{Ca}_{0.1})\text{CO}_3$ for the Dalroy rhodochrosite, and to $(\text{Ca}_{0.9}\text{Mn}_{0.1})\text{CO}_3$ for the manganous calcite. The presence of rhodochrosite was confirmed by X-ray powder diffraction analyses.

Genesis. The genesis of the cavity structures, the rhodochrosite itself and the deposit as a whole has not been satisfactorily resolved to date. However, probe analyses demonstrate that the baryte associated with the carbonate is enriched in Sr (up to 9.8 wt. %). This indicates a hydrothermal source, at least for the infill minerals, since the distribution of Sr-baryte is restricted to deposits of hydrothermal origin (Bonatti *et al.*, 1972).

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