Chapter 5

Spectroscopic Studies of Natural Mineral: Rhodochrosite
5.1 Introduction

Rhodochrosite (MnCO$_3$) is an important reduced phase mineral that occurs in terrestrial and marine deposits and sedimentary rocks [1-3]. The solubility limit of aqueous Mn concentration under anoxic conditions in many diverse environments [4]. Under oxic and mildly alkaline conditions, MnCO$_3$ solubility is complicated by oxidation of the released Mn(II) (aq) and subsequent precipitation of Mn$_{III/IV}$ (hydr)oxide mineral, which are orders of magnitude less soluble than the parent carbonate material [5]. Solubility may be further complicated by morphology: hysteresis in dissolution behavior occurs when (hydr)oxide minerals precipitate as insoluble coatings on the surfaces of carbonate grains and thus kinetically inhibit dissolution even in cases where carbonate dissolution is highly favored thermodynamically. Dissolution and precipitation are significant in the biogeochemical cycling not only of Mn but also of other metals (Eg. U, Co, Pb, Fe, Ni, Cu, and Zn) that co-precipitate with Mn (hydr)oxides [6].

In the natural environment, cycling of Mn occurs at oxic/anoxic interfaces where precipitation and dissolution occur simultaneously. Accurate understanding of biogeochemical cycling thus requires a quantitative description of the effects of O$_2$. Molecular oxygen (O$_2$) plays a critical role in determining the bioavailability of Mn due to the great solubility difference between Mn$_{III/IV}$ (hydr)oxides and Mn$_{II}$ carbonates. If equilibrium conditions prevail, understanding the effects of O$_2$ is straightforward: a thermodynamic analysis would provide both the mix of solids present and the aqueous (i.e., bio-available) concentration of Mn species. However, the equilibrium treatment fails for two important reasons. First, surface-controlled dissolution and precipitation rates may be slow. Second, morphologic features such as precipitation of an oxide supralayer may armor the carbonate surface and significantly reduce dissolution.
rates. Understanding the effects of O₂ on the dynamics of dissolution requires a kinetic chemical transport description.

Manganese is a pinkish-gray element, exists naturally in the environment and has chemically active nature. It is a key component of iron, steel production and widely used in alloys and fertilizers as catalyst. Manganese ions has d⁵ configuration and exist in different valence states (+2, +3, +4, +6 and +7) where as Mn(II) is the most stable oxidation state of manganese.

In view of this the present spectroscopic investigations of natural mineral sample rhodochrosite is carried out. The main purpose of the present study is to determine the valance state, site symmetry of Mn(II) ion and any other impurities present in the mineral.
5.2 Crystal Structure

Fig. 5.1 shows rhodochrosite natural mineral. A solid material whose constituents (atoms, molecules or ions) are arranged in a repeating pattern extending in three dimensions. Rhodochrosite is a naturally occurring manganese carbonate mineral with chemical composition MnCO$_3$. Quartz is also present in the specimen. In its pure form, it is typically a rose-red color, but impure specimens can be shades of pink to pale brown. The rhodochrosite crystal consists of repeating Mn(II) and CO$_3^{2-}$ in a repeating three dimensional pattern. It crystallizes in the trigonal system, and cleaves with rhombohedral carbonate cleavage in three directions. Fig. 5.2 shows the crystal structure of rhodochrosite.

![Fig. 5.1 Rhodochrosite natural mineral](image1)

![Fig. 5.2 Crystal structure of rhodochrosite](image2)
5.3 Experimental

Sample Collection

Rhodochrosite natural mineral sample was donated by Mr. Peter Brack, Institute of Mineralogy and Petrograph, ETH Zentrum, Switzerland and originated from Las Capilliters, Argentinean. Rhodochrosite sample could not be cut into single crystals, because of non-availability of sufficient quantity of the minerals.

Characterizations

Powder XRD pattern of the collected sample was recorded on PANalytical Xpert Pro diffractometer with CuKα radiation. Fine powdered mineral samples mixed with nujol (liquid paraffin) were used for optical absorption studies. The optical spectrum is recorded in the range from 400–2600 nm on JASCO V-670 spectrophotometer. The EPR spectra of the polycrystalline samples taken into EPR quartz tubes are recorded both at room and liquid nitrogen temperatures on JEOL–TE 100 ESR spectrometer operating at X-band frequency 8.985GHz. BRUKER ALPHA FT-IR spectrophotometer is used for recording FT-IR spectrum of rhodochrosite mineral in the region 500-4000 cm\(^{-1}\).
5.4 Theory

The electronic configuration of Mn(II) is (Ar) 3d⁵. It gives rise to ²S, ²P, ²D, ²F, ²H, ⁴P, ⁴D, ⁴F, ⁴G and ⁶S terms. The ground multiplet of Mn(II) ion is 3d⁵ ⁶S. Therefore, any crystalline field does not directly affect this state. To explain the ground level splitting, it is necessary to consider an admixing to ⁶S of higher multiplets and configurations which are split under the action of crystalline filed. In a cubic crystalline field of low to moderate strength, five d-electrons of Mn(II) ions are distributed in t₂g and e₉ orbitals with three in the former and two in the later. Thus the ground state configuration is t₂g³e₉². This configuration gives rise to the electronic states ⁶A₁g, ⁴A₁g, ⁴E₉, ⁴T₁g, ⁴T₂g and to a number of doublet states of which ⁶A₁g lies lowest according to Hund’s rule. The energy level for Mn(II) ions in octahedral environment is as follows: ⁶S → ⁶A₁g, ⁴G → ⁴T₁g + ⁴T₂g + ⁴E₉ + ⁴A₁g, ⁴D → ⁴T₂g + ⁴E₉, ⁴P → ⁴T₁g. The ⁴E₉ - ⁴A₁g (⁴G) and ⁴E₉ (⁴D) levels have relatively less influence compared to other levels by crystal filed [7]. Since, all excited states of Mn(II) ions (belonging to d⁵ configuration) will be either quartets or doublets. Energy level diagram of Mn²⁺ in a free ion state is shown in Fig. 5.3.

Crystal field (CF) is termed weak when its influence is lesser than that of spin orbit interaction and electronic repulsion, whereas it is strong when its influence is greater. If the CF influence is in between that of spin orbit and electronic repulsion, it is treated as intermediate field. The transitions ⁶A₁g → ⁴T₁g and ⁶A₁g → ⁴T₂g depends on the crystal field strength Dq and give rise to broad bands. For the transition like ⁶A₁g → ⁴E₉, which are independent of Dq the bands would be less broadened [8]. Splitting of EPR line in Mn(II) ion is shown in Fig. 5.4. Tanabe-Sugano diagram for d⁵ configuration is shown in Fig. 5.5.
Fig. 5.3 Energy level diagram of Mn(II) ions in a free ion state

\[ \text{Mn}^{2+} \text{ ion } I = 5/2 \]

\[ I_z \]

\[ \begin{array}{c}
\pm 5/2 \\
\pm 3/2 \\
\pm 1/2 \\
1/2 \\
3/2 \\
5/2 \\
5/2 \\
3/2 \\
1/2 \\
-1/2 \\
-3/2 \\
-5/2 \\
\end{array} \]

Fig. 5.4 Splitting of EPR line of Mn(II) ions owing to hyperfine interaction
Fig. 5.5 T-S diagram for octahedral $d^5$ electron configuration
5.5 Results and Discussion

5.5.1 Powder X-ray Diffraction Study

Fig. 5.6 shows powder XRD pattern of rhodochrosite sample depicted against the Bragg’s angle that ranged from 10° to 75°. The peak positions observed in Fig. 5.6 are well matched with standard diffraction data of JCPDS file no. 44-1472. The diffraction data is indexed to a rhombohedral crystal system and the corresponding lattice cell parameter are evaluated as a = 4.7806 Å and c = 15.7008 Å.

![Powder XRD pattern of rhodochrosite](image)

The average crystallite size of the collected sample is calculated by using Debye-Scherrer’s formula,

\[ D = \left( \frac{k\lambda}{\beta \cos \theta} \right) \]

where k is a constant (about 0.9), \( \lambda \) is wavelength of X-ray radiation (1.5405 Å), \( \beta \) is full width at half maximum (FWHM) intensity of the diffraction line and \( \theta \) is
diffraction angle. Based on the value of FWHM, the average crystallite size is estimated to be 57 nm, which is in the order of nanosize.

Accordingly, it is possible to calculate both of the strain $\varepsilon$, dislocation density $\delta$ to have more information about the structural characteristics of prepared sample. The average strain of collected sample was calculated by Stokes-Wilson equation $\varepsilon_{str} = \beta/4\tan\theta$ and dislocation density was calculated from the relation $\delta = 15\varepsilon/aD$.

$$\varepsilon_{str} = 0.1760 \times 10^{-3} \text{ and } \delta = 0.0963 \times 10^{15} \text{ lines/m}$$

5.5.2 Optical Absorption Study

The analysis of optical absorption spectrum is one of the most abundant tools for understanding and developing the electronic band structure of crystalline and non-crystalline materials. Electronic configuration of Mn(II) ions (d$^5$ configuration) gives rise to free ion terms $^6$S, $^4$P, $^4$F, $^4$G and number of doublet states of which $^6$S occupies the ground state. In crystal field, $^6$S and $^4$P terms split as $^6$A$_{1g}$ and $^4$T$_{1g}$ respectively. $^4$D and $^4$G splits into $^4$E$_g$+$^4$T$_{2g}$ and $^4$A$_{1g}$+$^4$E$_g$+$^4$T$_{1g}$+$^4$T$_{2g}$ respectively. Fig. 5.7 predicts the UV-Vis absorption spectrum of rhodochrosite natural mineral. The spectrum shows six characteristic bands at 306, 339, 362, 406, 449 and 563 nm are assigned to the transitions $^6$A$_{1g}$(S) $\rightarrow$ $^4$T$_{1g}$(P), $^6$A$_{1g}$(S) $\rightarrow$ $^4$E$_2$(D), $^6$A$_{1g}$(S) $\rightarrow$ $^4$T$_{2g}$(D), $^6$A$_{1g}$(S) $\rightarrow$ $^4$A$_{1g}$(G) + $^4$E$_g$(G), $^6$A$_{1g}$(S) $\rightarrow$ $^4$T$_{2g}$(G) and $^6$A$_{1g}$(S) $\rightarrow$ $^4$T$_{1g}$(G) respectively for Mn(II) ions. The nature and position of the bands shows the characteristic of Mn(II) ions in octahedral symmetry. The energy matrices for d$^5$ configuration with Tree’s correction factor ($\alpha = 76 \text{ cm}^{-1}$) are solved for various values of crystal field parameter (Dq) and Racah parameters (B and C), a good fit is obtained for Dq = 845, B = 830 and C = 2985 cm$^{-1}$. These values are in well consistent with previous reports [9]. The observed and calculated values are presented in Table 5.1. The evaluated crystal field and Racah parameters suggest
that the Mn(II) ions existed in rhodochrosite mineral as octahedral site symmetry.

![Fig. 5.7 Optical absorption spectrum of rhodochrosite](image)

**Table 5.1 Band head data and assignments of rhodochrosite natural mineral**

<table>
<thead>
<tr>
<th>Transition From $^6A_{1g}$</th>
<th>Band position</th>
<th>Wavelength (nm)</th>
<th>Wavenumber (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4T_{1g}(P)$</td>
<td></td>
<td>306</td>
<td>32670</td>
</tr>
<tr>
<td>$^4E_2(D)$</td>
<td></td>
<td>339</td>
<td>29490</td>
</tr>
<tr>
<td>$^4T_{2g}(D)$</td>
<td></td>
<td>362</td>
<td>27616</td>
</tr>
<tr>
<td>$^4A_{1g}(G) + ^4E_2(G)$</td>
<td></td>
<td>406</td>
<td>24685</td>
</tr>
<tr>
<td>$^4T_{2g}(G)$</td>
<td></td>
<td>449</td>
<td>22271</td>
</tr>
<tr>
<td>$^4T_{1g}(G)$</td>
<td></td>
<td>563</td>
<td>17757</td>
</tr>
</tbody>
</table>

113
5.5.3 EPR Study

It provides a detailed description of the ground state of paramagnetic ions and enables to understand the nature of site symmetry produced by ligands around the transition metal ion. Mn(II) ions belongs to d\textsuperscript{5} configuration and it is well known that axial distortion of octahedral symmetry gives rise to three Kramer’s doublets in the case of Mn\textsuperscript{2+}, i.e., |\pm5/2>, |\pm3/2> and |\pm1/2>. Application of Zeeman field lifts spin degeneracy of the Kramer’s doublets [10]. As \textsuperscript{55}Mn hyperfine interaction is large and very anisotropic in low-spin Mn(II) ion complexes, isotropic spectra tend to be poorly resolved and undiluted powders give very broad lines. EPR spectra of low-spin Mn(II) ion complexes have been elusive, in part because of high-spin Mn(II) ions decomposition products which have easily observed spectra. A typical X-band EPR spectrum, observed at room temperature for rhodochrosite is shown in Fig. 5.8, which has broad line centered at g = 2.0981, characteristic of distorted octahedral site symmetry of Mn(II) ions.

![EPR spectrum of rhodochrosite](image_url)

**Fig. 5.8 EPR spectrum of rhodochrosite**
The hyperfine splitting (A) parameter is evaluated as $A = 123 \times 10^{-4}$ cm$^{-1}$. The value of “A” nearer to $100 \times 10^{-4}$ cm$^{-1}$ is consistent with Mn(II) ions in octahedral coordination [11]. The g-value for the hyperfine splitting is indicative of nature of the bonding. If the g-value shows a negative shift with respect to the free electron value (2·0023) then the bonding is ionic and conversely, if the shift is positive, then the bonding is more covalent in nature. In the present case the bonding between Mn(II) ions and its carbonates is covalent.

5.5.4 FT-IR Study

FT-IR spectroscopy was used to investigate the functional groups of rhodochrosite (MnCO$_3$). The corresponding spectrum of rhodochrosite is given in the Fig. 5.9, from this three sharp carbonate bands observed at 724, 864, 1418 cm$^{-1}$ and with a little peak at 1798 cm$^{-1}$. The peak at 1798 cm$^{-1}$ is due to the C=O stretching vibration [12]. The peak at 724 cm$^{-1}$ assigned to In-plane bending vibration of CO$_3^{2-}$ ($\nu_4$), 864 cm$^{-1}$ attributed to out-of-plane bending vibration of CO$_3^{2-}$ ($\nu_2$) and Asymmetric stretching vibration of CO$_3^{2-}$ is observed at 1418 cm$^{-1}$ [13, 14]. The fundamental vibrational modes of rhodochrosite mineral are assigned and are presented in Table 5.2.

Table 5.2 Vibrational band assignments of rhodochrosite mineral

<table>
<thead>
<tr>
<th>Vibrational frequency (cm$^{-1}$)</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1798</td>
<td>C=O stretching vibration</td>
</tr>
<tr>
<td>1450</td>
<td>$\nu_3$, Asymmetric stretch of CO$_3^{2-}$</td>
</tr>
<tr>
<td>862</td>
<td>$\nu_2$, Out-of-plane bend of CO$_3^{2-}$</td>
</tr>
<tr>
<td>735</td>
<td>$\nu_4$, In-plane bend of CO$_3^{2-}$</td>
</tr>
</tbody>
</table>
Fig. 5.9 FT-IR spectrum of rhodochrosite
5.6 Conclusions

- From powder XRD pattern of rhodochrosite sample, the diffraction data is indexed to a rhombohedral crystal system with JCPDS file no. 44-1472 and the corresponding lattice cell parameter are evaluated as \( a = 4.7806 \, \text{Å} \) and \( c = 15.7008 \, \text{Å} \).

- The average crystallite size is evaluated as 57 nm. Microstrain and dislocation density are evaluated as \( \varepsilon_{\text{str}} = 0.1760 \times 10^{-3} \) and \( \delta = 0.0963 \times 10^{15} \) lines/m.

- Optical absorption spectrum exhibits six characteristic bands of Mn\(^{2+}\) ions with distorted octahedral site symmetry in rhodochrosite mineral. Crystal field and Racah parameters are evaluated.

- A typical X-band EPR spectrum is observed at room temperature for rhodochrosite has broad line centered at \( g = 2.0981 \), characteristic of distorted octahedral site symmetry of Mn(II) ions. The hyperfine splitting \( (A) \) parameter is evaluated as \( A = 123 \times 10^{-4} \, \text{cm}^{-1} \). The value of “\( A \)” nearer to 100 \( \times 10^{-4} \, \text{cm}^{-1} \) is consistent with Mn\(^{2+}\) in octahedral coordination. The bonding nature between Mn(II) ions and its carbonates is covalent.

- FT-IR spectrum exhibited various vibrational bands characteristic of C=O stretching vibration and carbonate bands.
5.7 References


