Oxidation character of chlorite from Byrapur chromite deposit, India – A ^{57}Fe Mössbauer evaluation

TAPAN PAL, PRABAL KUMAR MAITY, DIPANKAR DAS* and SACHINATH MITRA

Department of Geological Sciences, Jadavpur University, Calcutta 700032, India

*Department of Solid State Physics, Indian Association for the Cultivation of Science, Calcutta 700032, India

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Abstract. Chlorite occurring in tremolite-chlorite schist rock of Byrapur chromite deposit of southern India has been investigated by ^{57}Fe Mössbauer spectroscopy along with XRD, IR and EPMA analyses. From XRD and EPMA results the chlorite is identified as clinocllore. The fit of Mössbauer spectrum (at room temperature) shows five symmetric doublets for iron. Based on hyperfine parameters three doublets are assigned to Fe^{2+} at *trans* and *cis* positions of talc layers, and Fe^{2+} at brucite layer. The remaining two doublets are attributed to Fe^{3+} at *trans* position and Fe^{3+} at tetrahedral site. The Mössbauer result suggests that the Fe^{3+} in octahedral sites of this chlorite was caused by oxidation after chloritization. The chlorite of Byrapur area was less oxidized compared to the chlorite of Sukinda chromite deposit of eastern India.

Keywords. Oxidation character; chlorite; Mössbauer spectroscopy.

1. Introduction

Chlorite, a phyllosilicate, occurs in two varieties: (a) dioctahedral and (b) trioctahedral. Most chlorites found in nature are of trioctahedral where the tetrahedral–octahedral–tetrahedral (T–O–T) silicate layers are bonded together by hydroxide sheets. The T–O–T layers (known as talc layers) and hydroxide sheets (known as brucite layers) may be represented as $(\text{R}^{2+}, \text{R}^{3+})_3[\text{Si}_{4-x}\text{Al}_x]\text{O}_{10}(\text{OH}_2)$ and $(\text{R}^{2+}, \text{R}^{3+})_3(\text{OH})_6$ respectively, where R can be Mg, Fe^{2+} , Fe^{3+} , Al, Mn, etc. and () represents octahedral sites while [] represents tetrahedral sites. In T–O–T silicate layers the cations are octahedrally coordinated by four O^{2-} anions and two OH^- groups in *cis* or *trans* positions (see for example, Bailey 1984) (figure 1).

Using ^{57}Fe Mössbauer spectroscopy, the valence and coordination of Fe species at different sites of the chlorite structure have been evaluated by various workers (Goodman and Bain 1979; Blaauw *et al* 1980; Kodama *et al* 1982; Ballet *et al* 1985; Townsend *et al* 1986; De Grave *et al* 1987; Pal *et al* 1992). Mössbauer studies down to 4.2 K reveal that in chlorite, magnetic ordering takes place below 7 K (Townsend *et al* 1986). Recently, Pal *et al* (1992) studied diabantite chlorite samples collected from Sukinda chromite deposit of eastern India and showed that the vulnerability of oxidation of the Fe at different octahedral sites could be correlated with the degree of distortion of the corresponding sites.

In the present paper we report the Mössbauer analysis of a trioctahedral chlorite from tremolite-chlorite rock of Byrapur ($13^\circ 07'\text{N}$; $76^\circ 55'\text{E}$) chromite deposit in southern India. The Mössbauer results have been supplemented by XRD, IR and EPMA analyses. Due to similar petrologic characters of Sukinda and Byrapur chromite deposits the obtained Mössbauer results of Byrapur chlorite have been compared with

our earlier reported results (Pal *et al* 1992) on Sukinda chlorite. Such comparison enables us to assess the oxidation behaviour of chlorites from widely separated areas.

2. Field characters

In Byrapur area chromite-bearing ultramafic intrusive occurs in the Archeans of Peninsular India. The ultramafic rocks are altered primarily to serpentinite, serpentine-talc-chlorite schist; the grade of metamorphism increases from green schist to amphibolite facies along this belt (*cf.* Ramakrishnan 1981). The chromitite bodies occur commonly as layers, high angle bands and in tabular or lensoid form.

The chromite-bearing ultramafic belt of Sukinda lying beyond the southern fringe of Singhbhum craton is the largest chromite deposit of India. The ultramafic rocks have been altered to serpentinite, talc-tremolite-chlorite schist and a monomineralic chlorite rock. The chromite deposit has been delineated to two horizons on the basis of physicochemical properties (Mitra 1960, 1976). Layers/bands, pockets and disseminations are the usual mode of the occurrence of chromitites.

3. Experimental

The flakes of chlorite mineral, after separation from talc-chlorite schist rock by binocular microscope, were rinsed in acetone and pulverized in an agate mortar avoiding hard-pressing. The powder was used for XRD, IR and ^{57}Fe Mössbauer spectroscopic investigations. The polished samples of tremolite-chlorite schist were used for chemical study using electron probe microanalyser (EPMA).

The XRD study was carried out in a microprocessor-controlled Philips X-ray diffractometer (PW 1710) using Cu-K_α radiation and Ni-filter. The IR spectrum was recorded by an Elmer-597 spectrometer using KBr disc method. To minimize the orientation effect in ^{57}Fe Mössbauer study, the powdered sample was mixed with sugar and ground under acetone in an agate mortar. Later on the dried powder sample was used for Mössbauer study. The Mössbauer spectrum was recorded in a Wissel make conventional constant acceleration Mössbauer spectrometer with a ^{57}Co (in Rh) source of ~ 10 mCi strength. The spectrometer was calibrated against a high purity natural iron foil of $25\ \mu\text{m}$ thickness (supplied by Amersham International Plc.). The spectrum was fitted by using a modified version of the least squares fitting programme of Meerwall (1975) on an IBM personal computer. For all the peaks Lorentzian line shape was assumed.

EPMA was carried out on polished samples using JEOL-733 superprobe micro analyser with wavelength dispersive method at 15 kV with beam current of $0.01\ \mu\text{A}$. Natural silicate of standards were used for calibration.

4. Results and discussion

4.1 XRD study

From the positions and intensities of the strongest peaks of X-ray diffractogram (figure 1) the samples are identified as clinocllore species of chlorite. The presence of (060) peak at $1.53\ \text{\AA}$ indicates trioctahedral nature of this chlorite (*cf.* Mitra 1989).

Figure 1. Schematic representation of the chlorite structure projected on (010) plane and showing the sequence of silicate layers and hydroxide sheets.

The cell parameters calculated from X-ray peaks are $a = 5.32 \pm 0.003$, $b = 9.28 \pm 0.002$, $c = 14.24 \pm 0.007$ and $\beta = 97.7^\circ \pm 0.04$.

4.2 EPMA study

The microprobe analysis reveals an apparent homogeneity in the chemical character of the sample (table 1) and indicates these as clinochlore, as classified by Bailey *et al* (1979).

4.3 IR study

The infrared spectrum of the representative sample (figure 2) was recorded in $4000\text{--}200\text{ cm}^{-1}$ region. The IR spectra of the chlorite and serpentine groups are similar but the Si–O stretching band around 990 cm^{-1} characterizes it as chlorite. The band at 3560 cm^{-1} marks the presence of OH in the 2:1 layer and 3380 cm^{-1} band, characteristic of trioctahedral chlorite, is ascribed to interlayer OH (*cf.* Shirozu 1985). The band at 760 cm^{-1} may be caused by tetrahedral Al (Farmer 1974). The single band at that region may be a composite band involving OH libration and lattice vibration (Shirozu 1985). The band at $360\text{--}460\text{ cm}^{-1}$ is ascribed to M–O stretching vibration (Adams 1967).

4.4 ^{57}Fe Mössbauer investigation

The Mössbauer spectrum recorded at room temperature (297 K) shows an asymmetric envelope with more intense peak at lower velocity side. Because of strong basal cleavage the flakes of chlorite tend to align along the plane of the absorber. Since the principal axis of EFG is along c -axis, the angle between it and the incident γ -rays is not at random; this causes asymmetry in the spectra, the largest line of which lies in the negative velocity side. Sometimes, this texture-induced asymmetry can be avoided by magic-angle ($\gamma \wedge c = 54.79^\circ$) mounting of the absorber (*cf.* Mitra 1992).

Table 1. Electron microprobe analyses of chlorite.

Sample	BC-4	BC-7	BC-8
SiO ₂	27.69	26.74	27.42
TiO ₂	0.02	0.06	0.05
Al ₂ O ₃	22.26	21.77	22.11
Cr ₂ O ₃	0.07	0.08	0.09
FeO	12.26	11.72	12.28
MnO	0.17	0.17	0.15
MgO	24.56	24.36	24.72
NiO	0.01	0.09	0.07
CaO	0.01	0.01	0.01
Total	87.05	85.00	86.90
Cations calculated on 14 oxygen basis			
Si	2.725	2.703	2.712
Ti	0.001	0.004	0.002
Al	2.589	2.593	2.582
Cr	0.005	0.006	0.008
Fe ³⁺	0.377	0.366	0.376
Fe ²⁺	0.633	0.624	0.641
Mn	0.012	0.014	0.012
Mg	3.611	3.671	3.647
Ni	0.001	0.007	0.005
Ca	0.001	0.001	0.001

In EPMA analyses total iron was calculated as FeO but total iron was distributed into Fe²⁺ and Fe³⁺ from the Fe³⁺/Fe²⁺ ratio obtained in Mössbauer result.

Structural formulas of the chlorite:

The fitting with five doublets offer an acceptable χ^2 value (0.96) and accounts for the area under the envelope (with its asymmetric form). The spectrum was fitted by three approaches (table 2) viz. (a) three-doublet-fit with one doublet assigned to octahedral Fe³⁺ and other two for octahedral Fe²⁺, (b) four-doublet-fit with two doublets for Fe³⁺ and other two for octahedral Fe²⁺, and (c) five-doublet-fit with two for Fe³⁺ and remaining three corresponding to octahedral Fe²⁺.

Table 2 shows that the three-doublet-fit (*cf.* Bancroft 1973) model shows poor χ^2 (1.8) and linewidths. The four-doublet-fit shows better χ^2 (1.2) than three-doublet-fit but shows large linewidth for Fe³⁺ (0.69 mm/s). The five-doublet-fit shows reasonably good χ^2 (0.96) which is better than that for four-doublet-fit as well as with acceptable linewidths for the iron doublets in natural minerals. The five-doublet-fit was, therefore, preferred to other models and the results are discussed on that basis.

Out of the five doublets, those showing isomer shifts (IS) 1.01 mm/s, 1.10 mm/s and

Figure 2. The X-ray diffractogram of Byrapur chlorite (BC-4).

Table 2. Mössbauer parameters of chlorites at room temperature.

Area		Isomer shift (IS) (mm/s)	Quadrupole splitting (QS) (mm/s)	Linewidth (Γ) (mm/s)	Distribution	Relative area (%)	χ^2	$\text{Fe}^{3+}/\text{Fe}^{2+}$
Byrapur	'Three doublet fit'	1.17	2.82	0.22	Fe^{2+}	14	1.8	0.72
		1.10	2.46	0.39	Fe^{2+}	44		
		0.32	0.61	0.92	Fe^{3+}	42		
	'Four doublet fit'	1.24	2.65	0.28	$\text{Fe}^{2+}(\text{T})$	23	1.2	0.53
		1.07	2.67	0.30	$\text{Fe}^{2+}(\text{C})$	27		
		0.91	2.49	0.29	$\text{Fe}^{2+}(\text{B})$	15		
		0.42	0.44	0.69	$\text{Fe}^{3+}(\text{C})$	35		
	'Five doublet fit'	1.14	2.89	0.25	$\text{Fe}^{2+}(\text{B})$	19	0.96	0.58
		1.10	2.55	0.26	$\text{Fe}^{2+}(\text{C})$	30		
		1.01	2.25	0.33	$\text{Fe}^{2+}(\text{T})$	14		
		0.42	0.80	0.45	$\text{Fe}^{3+}(\text{T})$	20		
		0.29	0.30	0.45	$\text{Fe}^{3+}(\text{tet})$	17		
Sukinda		1.12	2.55	0.32	$\text{Fe}^{2+}(\text{C})$	16	1.47	0.78
		1.10	2.59	0.31	$\text{Fe}^{2+}(\text{B})$	21		
		0.33	0.65	0.36	$\text{Fe}^{3+}(\text{T})$	30		
		0.33	0.40	0.32	$\text{Fe}^{3+}(\text{C})$	33		

B – brucite site, C – *cis* site, T – *trans* site and tet – tetrahedral site.

1.14 mm/s are due to Fe^{2+} at octahedral coordination (Bancroft 1973). The remaining doublets having IS values 0.29 mm/s and 0.42 mm/s are due to Fe^{3+} in tetrahedral and octahedral coordinations respectively (Bancroft 1973).

The difference in QS values of the *cis* and *trans* sites is 0.30 mm/s, which is small compared to other phyllosilicates having Fe^{2+} only at *cis* and *trans* sites (e.g. glaucophene, biotite etc). The third Fe^{2+} doublet can be attributed to brucite layer, which

Figure 3. Infrared spectrum of Byrapur chlorite (BC-4).

Figure 4. Room temperature ^{57}Fe Mössbauer spectrum of Byrapur chlorite (BC-4).

should have a greater QS than *cis* and *trans* sites in accordance with the quasiempirical rule. These hyperfine values indicate that the Fe^{2+} ions in all the three coordinations exhibit an electronic singlet ground state (Ingalls 1964), which characterizes compressed octahedra (vide Mitra 1992).

Assuming the same Lamb Mössbauer factor for both Fe^{2+} and Fe^{3+} ions irrespective of the sites, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (table 2) is calculated from corresponding peak areas.

The distribution pattern of Fe^{2+} cations in different sites of the chlorite structure is not very clearly known. The ^{57}Fe Mössbauer and neutron diffraction studies show that Fe^{2+} can occur in all the three available octahedral sites (Taylor *et al* 1968; Coey 1975; Goodman and Bain 1979; Kodama *et al* 1982; Ballet *et al* 1985; De Grave *et al* 1987; Pal *et al* 1992). From Mössbauer result it was suggested earlier that although the *cis* and brucite sites have similar order of distortion, the *cis* site is slightly more distorted than brucite site (Pal *et al* 1992).

The distribution of Fe^{2+} in octahedral sites of chlorite structure is usually made on the basis of quadrupole splitting (QS) values (Goodman and Bain 1979; De Grave *et al* 1987). It is known that for Fe^{2+} larger distortion of octahedral sites results in smaller QS values (Bancroft 1973). The Fe^{2+} doublet with QS 2.25 mm/s is, therefore, assigned to *trans* site. The *cis* site being more distorted than brucite site should have a lower QS than that for a brucite site. Thus the doublet showing QS 2.55 mm/s is assigned to Fe^{2+} at *cis* site and the doublet with QS 2.89 mm/s is assigned to Fe^{2+} at brucite site.

The QS values of Fe^{3+} in octahedral site increase with increase of site distortion in contrast to Fe^{2+} behaviour (Bancroft 1973). The observed QS value for Fe^{3+} at octahedral site (0.81 mm/s) is higher than the earlier reported QS values for *trans* site (e.g., ~ 0.65 mm/s, Kodama *et al* 1982; Pal *et al* 1992). That doublet is, therefore, more likely due to Fe^{3+} at *trans* site. The observed QS value is more or less the same as reported for oxidized chlorite (~ 0.82 mm/s) by Kodama *et al* (1982).

The doublet with IS 0.29 mm/s and QS 0.30 mm/s indicates that it is due to Fe^{3+} at tetrahedral site (Bancroft 1973). Tetrahedral Fe^{3+} in chlorite is not common but can occur in some cases as reported by Goodman and Bain (1979).

5. Oxidation history

The present investigation shows that in Byrapur chlorite Fe^{2+} has occurred in all three octahedral sites i.e. *trans*, *cis* and brucite sites and Fe^{3+} has occurred in octahedral *trans* site and tetrahedral site. The occurrence of Fe^{3+} at tetrahedral site may be related to higher Al content of the present chlorite, as observed in case of aluminous orthopyroxene (*cf.* Annersten *et al* 1978).

The Mössbauer study on the trioctahedral chlorite of Sukinda area (table 2) shows that *trans* site contains iron only as Fe^{3+} , the *cis* site contains both Fe^{2+} and Fe^{3+} and brucite site contains iron only in Fe^{2+} form. The presence of Fe^{3+} at octahedral site(s) of chlorite as found both in Sukinda and Byrapur chromite deposits may be due to the following reasons:

- (a) Fe^{3+} was originally present in the primary silicates from which the chlorite had formed and was thus incorporated in chlorite structure.
- (b) Only Fe^{2+} was present in the primary silicates and was converted into Fe^{3+} during alteration of primary silicates and was incorporated in chlorite structure.
- (c) Oxidation of Fe^{2+} , present in chlorite subsequent to chlorite formation.

Amongst these three possibilities the first two are unlikely, because if Fe^{3+} was incorporated into the chlorite structure Fe^{3+} ($r = 0.64 \text{ \AA}$) due to smaller ionic radius than Fe^{2+} ($r = 0.78 \text{ \AA}$) would preferentially go to the least distorted site i.e. brucite site (*cf.* Pal *et al* 1992). But the Mössbauer results show that Byrapur chlorite contains

Fe^{3+} only in the *trans* site and the Sukinda chlorite contains Fe^{3+} only in *trans* and *cis* sites but not in the brucite site. It is, therefore, more probable that Fe^{3+} had formed during oxidation of Fe^{2+} to Fe^{3+} at a stage when the formation of chlorite (i.e. chloritization) from primary silicates was over. In Sukinda chlorite the oxidation ($\text{Fe}^{2+} - 1e \rightarrow \text{Fe}^{3+}$) was complete in *trans* site and was partial in *cis* site, whereas brucite site remained unaffected. The oxidation was partial only in *trans* site of Byrapur chlorite. From this aspect, as well as smaller $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of Byrapur chlorite than that of Sukinda chlorite, it is evident that the former was oxidized at lower oxygen fugacity level than the latter.

6. Conclusion

The Mössbauer study of Byrapur chlorite shows that at *trans* position iron has occurred both as Fe^{2+} and Fe^{3+} , but *cis* and brucite sites contain iron only as Fe^{2+} ion. The iron distribution over the octahedral sites imprints partial oxidation of Fe^{2+} only at *trans* site. The Mössbauer study of Byrapur chlorite as well as Mössbauer result of chlorite of Sukinda chromite deposit suggest that Fe^{3+} enrichment in chlorites of both the areas was caused by the oxidation at a later stage of chloritization. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio as well as Fe^{2+} and Fe^{3+} distribution show that Byrapur chlorite was less affected by oxidation than that of Sukinda area.

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