Structural modifications in natural tremolites: Spectroscopic studies

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Two near-end members of calcic-amphiboles collected from metamorphic regions were characterized using electron probe micro analysis (EPMA), vibrational spectroscopy (micro-Raman and FTIR) and electron (spin) paramagnetic resonance (EPR) techniques. Both the amphiboles were found to be tremolites with the 'A' site being partially occupied by Na and K. The characteristic vibrational modes of tremolites were observed in micro-Raman and FTIR studies. Additionally, the coexistence of amphiboleand pyroxene-like bands in the range 3000-3800 cm⁻¹ in FTIR indicates that these tremolites would have undergone some structural modifications. EPR showed the presence of paramagnetic manganese (Mn²⁺) and iron (Fe³⁺) ions. From the intensity ratios of Mn²⁺ hyperfine spectral lines, the crystal field distortion parameter D was estimated to be $(8.5 \pm 2.0) \times$ $10^{-3} \, \text{cm}^{-1}$ and $(9.2 \pm 2.0) \times 10^{-3} \, \text{cm}^{-1}$, respectively, for both the samples. These observations corroborate the induced structural modifications in these tremolites.

AMPHIBOLES are widely used as indicators to unravel various igneous and metamorphic processes in a geological formation. Detailed spectroscopic investigations on natural samples would delineate the induced structural modifications due to various geological processes. Amphiboles are generally classified on the basis of their unit cell dimensions and contents¹. A large number of cations could be accommodated in the amphiboles as trace elements and their presence has a vital role in the stability of the crystal structure^{1,2}. Generally the size of the cations, their occupancy on different sites and the ability to exist in various oxidation states induce disorder into the crystal structure³. The vibrational spectroscopic (IR and Raman) techniques are versatile in probing the structural arrangement, in particular, the presence of hydroxyl ions in amphiboles are better clucidated by these techniques. Electron paramagnetic resonance (EPR) is a powerful and non-destructive tool in detecting the paramagnetic trace elements present in the samples in any form, i.e. crystal, powder or polycrystalline aggregates. On the other hand, fine and hyperfine spectra of trace elements could be used to probe the structural changes and crystal field effects⁴.

Earlier infrared spectroscopic studies on amphiboles were mostly confined to the fundamental stretching region of the hydroxyl group around 3600-3700 cm⁻¹ (refs 5 and 6). However, other modes of silicate chain network could be used for identification⁷. Raman spectroscopy of tremolites are limited in literature⁸; a useful tool to characterize the basic molecular linkages and induced disorder (positional and orientational). The EPR technique was used extensively to detect the trace elements and defects in minerals and rocks⁹. The presence of Mn²⁺ ion in natural tremolite has been well documented^{10,11}. Further, very few reports of EPR deal with the presence of Fe³⁺ ion in tremolite¹². However, Mössbauer spectroscopy is a well-established technique to estimate the disorder effects connected with ferrous and ferric ions¹. In this report, we present our spectroscopic studies on two natural amphiboles collected from different geological locations.

The samples are in a polycrystalline aggregate form and a small suitable section of each sample was used as such in the spectroscopic studies. The micro-Raman studies were carried out on a SPEX triplemate system, coupled with a cooled CCD detector and a SPECTRA PHYSICS argon ion laser for exciting the sample. For FTIR studies we used a NICOLET 740 spectrometer. The EPR spectra were recorded on a Varian spectrometer in the X-band region with a frequency of about 9.5 GHz.

Large variations in the mineral contents of the metasedimentary rocks of the Rajasthan region along the strike and stratification indicated that the variation is due to metamorphic impress on sedimentary rocks with sharp changes in facies from pure marble through tremolite marble, different grades of metamorphism have been reported ^{13,14}. Sample I of the present study was collected from this region while sample II of Puralia region was supplied by M/s Hindustan Minerals and Natural History Specimen Supply Co., Calcutta. The present study on tremolite derived from marbles is aimed at understanding the structural modifications caused due to the regional metamorphism.

A properly polished thin section of the sample was analysed using EPMA. The average percentage weights of the oxides are given in Table 1. The number of cations in Table 1 were calculated assuming 23 oxygen atoms and following the procedure of Deer et al.³. Results of the analysis indicate that Ca²⁺ (1.53, 1.72), Mg²⁺ (4.87, 5.06) and Si⁴⁺ (7.70, 7.93) are present as major cations. The other cations Na⁺, K⁺, Al³⁺, Fe, Mn²⁺, Ti⁴⁺, Cr³⁺ and Ni²⁺ are in minor quantities indicating the ability of the amphibole structure to accommodate ions of different radii. Petrological observation and EPMA analysis of the matrix reveal that these amphiboles were embedded in a dolomite rock. Small fibrous grains of amphiboles were observed in random in the host rock. The general chemical formula of tremolite is

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 $[A_{0-1}B_2C_5T_8\ O_{22}\ (OH,\ F,\ Cl)_2]$, where A is Na, K; B is Na, Li, Ca. Mn, Fe, Mg; C is Mg, Mn, Al, Fe, Ti and T is Si. Al. The chemical formulae were calculated using the oxide weight percentages found in EPMA analysis as in Table I and by normalizing the cations in groups¹⁵. The resultant chemical formulae for samples I and II are $[(Na_{0.12}, K_{0.01}) (Ca_{1.53}, Mg_{0.39}, Fe, Mn)_2 (Mg_{4.49}, Al, Fe)_5]$ $(Si_{7.70}, Al)_8 O_{22} (OH, Cl, F)_2$ and $[(Na_{0.02}, K_{0.01}) (Ca_{1.72}, K_{0.01})]$ $Mg_{0.01}$, Fe, Mn)₂ ($Mg_{4.95}$, Ti, Cr, Ni)₅ (Si_{7.93}, Al, Fe)₈ O₂₂ (OH, Cl, F)₂], respectively. In this analysis we did not differentiate between ferric and ferrous ions. It is interesting to note that the total Si and Al cations exceeds 8, that could be accommodated on a tetrahedral site in sample I, whereas it is less in sample II, giving scope for cationic disorder on the T site. The T group cationic deficiency in sample II could be filled in by Fe³⁺, whereas excess Al ions in sample I could occupy sites of C group ions. The ratio of $(Ca/\sum M)$ in both the samples is about 0.269 and 0.323, respectively, and is close to that of an ideal tremolite (0.3) (ref. 1).

Figure 1 shows the recorded Raman spectra of sample I and sample II up to $1200 \,\mathrm{cm^{-1}}$. Strong fluorescent background completely masked the other vibrational modes above $1200 \,\mathrm{cm^{-1}}$. It is clear from Figure 1 that the main Raman bands in samples I and II are at 670, 218, 155, 118 cm⁻¹ and 670, 221, 159, 118 cm⁻¹, respectively. The characteristic strong Raman band of tremolites observed at around 670 cm⁻¹ has been assigned to ν_s (T-O-T). It is worth noticing that the corresponding Raman band for pyroxenes occurs at around 650 cm⁻¹. Other weaker Raman bands observed in the present study are comparable with that reported earlier for tremolites.

Infrared spectra of both the samples in the range of 400-4000 cm⁻¹ are shown in Figure 2. Each spectrum is

Table 1. EPMA analysis of natural tremolites

Oxide	Av % weight		No. of cations	
	(1)	(II)	(I)	(II)
SiO ₂	56.863	56.647	7.692	7.933
Al_2O_3	3.267	0.311	0.520	0.050
FeO	2.304	1.647	0.260	0.186
MnO	0.049	0.050	0.006	0.006
MgO	24.167	25.087	4.870	5.056
CaO	10.531	11.877	1.525	1.720
TiO ₂	0.059	0.013	0.006	0.001
Na ₂ O	0.451	0.061	0.118	0.016
K ₂ O	0.073	0.040	0.012	0.007
Cr ₂ O ₃	0.024	0.186	0.0001	0.019
NiO	100.0	0.030	1000.0	0.003

Calculations are made by assuming 23 oxygen atoms. Chemical composition from EPMA analysis for sample I is $[(Na_{0.12}, K_{0.01})]$ (Ca_{1.53}, Mg_{0.39}, Fe, Mn)₂ (Mg_{4.49}, Al, Fe)₅ (Si_{7.70}, Al)₈ O₂₂ (OH, Cl, F)₂] and for sample II is $[(Na_{0.02}, K_{0.01})]$ (Ca_{1.72}, Mg_{0.01}, Fe, Mn)₂ (Mg_{4.95}, Ti, Cr, Ni)₅ (Si_{7.93}, Al, Fe)₈ O₂₂ (OH, Cl, F)₂].

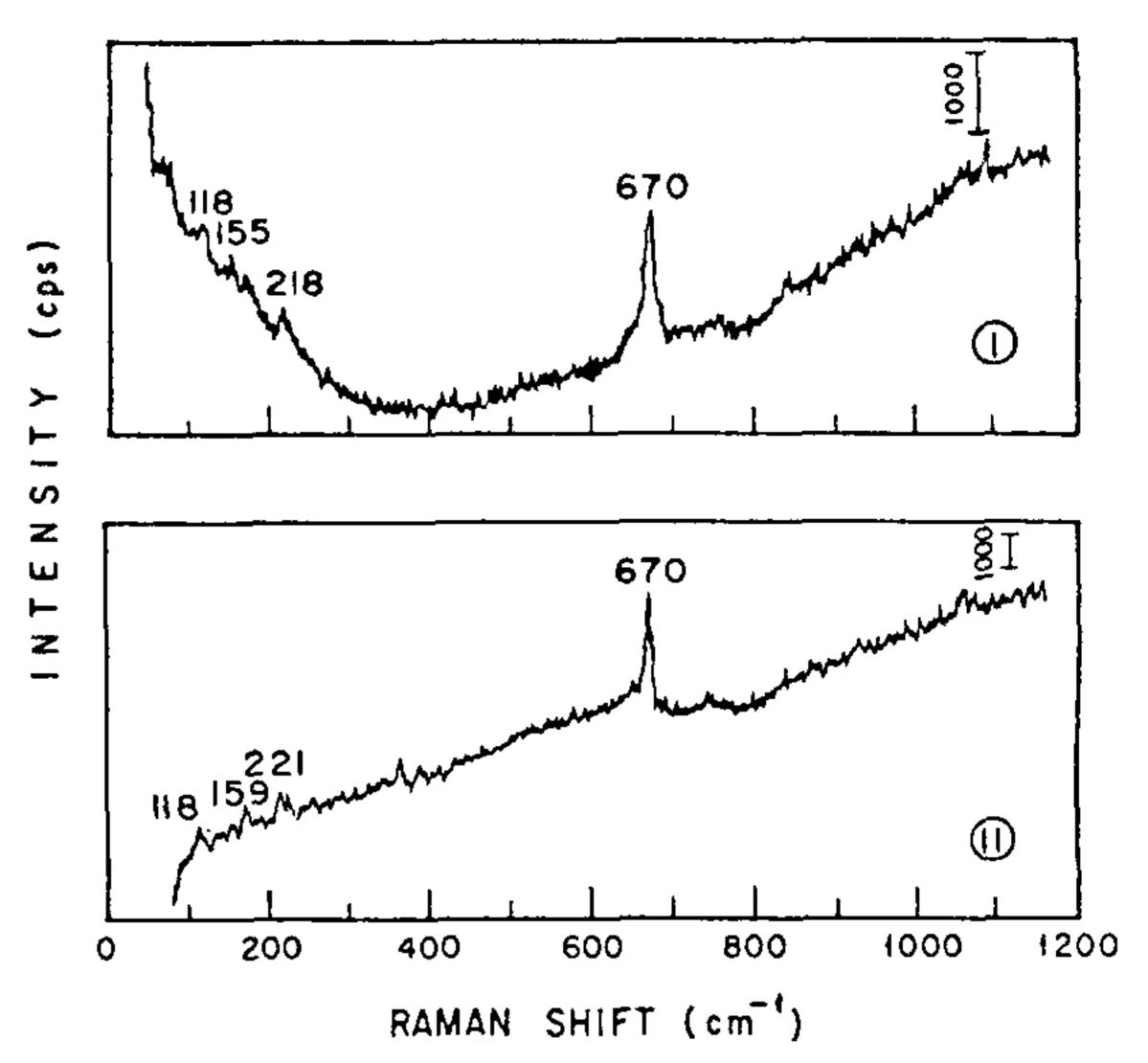


Figure 1. Micro-Raman spectra of natural tremolite.

the resultant of 32 scans. The samples as such were mixed with KBr to prepare a pallet and hence in the spectra the bands of host rock might overlap with that of tremolites. Indeed a stronger band at 1427 cm⁻¹ and a weaker one at 876 cm⁻¹ in both the samples could be due to dolomite. Other infrared bands observed in both these samples are comparable with the documented values'. Particularly the band around 640 cm⁻¹ has been correlated inversely with the weight % of FeO contents¹. From Figure 2 it is clear that this band was observed at around 668 cm⁻¹ indicating the presence of a small amount of FeO. Indeed the observed FeO weight % in samples I and II are about 2.30 and 1.65, respectively (see Table 1). It is generally accepted that Mg occupies M(1), M(2) and M(3) sites in amphiboles¹. It was established that the 640 cm⁻¹ band in the IR spectra further correlated with the occupancy of these sites by other trace elements like Fe, Mn, Ti and Al^I. In other words, this band occurs at higher wave number if the ratio of $\{Mg/(Mg + \Sigma M)\}$ approaches unity. This ratio in samples I and II is 0.95 and 0.97, respectively; and the appearance of IR band at around 668 cm⁻¹ strongly corroborates the lower occupation probability of these sites by other trace elements. Other IR modes observed in the present study at around 757, 920, 954, 1017 and 1098 cm⁻¹ in both the samples compare well with the tremolite bands documented elsewhere 1.17.

Furthermore, the (OH) symmetric stretching mode region in the IR spectra of amphiboles has extensively been studied^{1,5}. The observed fine structure of this band has been attributed to local ordering and site occupancy of trace elements. Figure 3 shows the IR spectra of both samples in the range 3000–3800 cm⁻¹. In both the samples we observed a sharp band around 3674 cm⁻¹, which

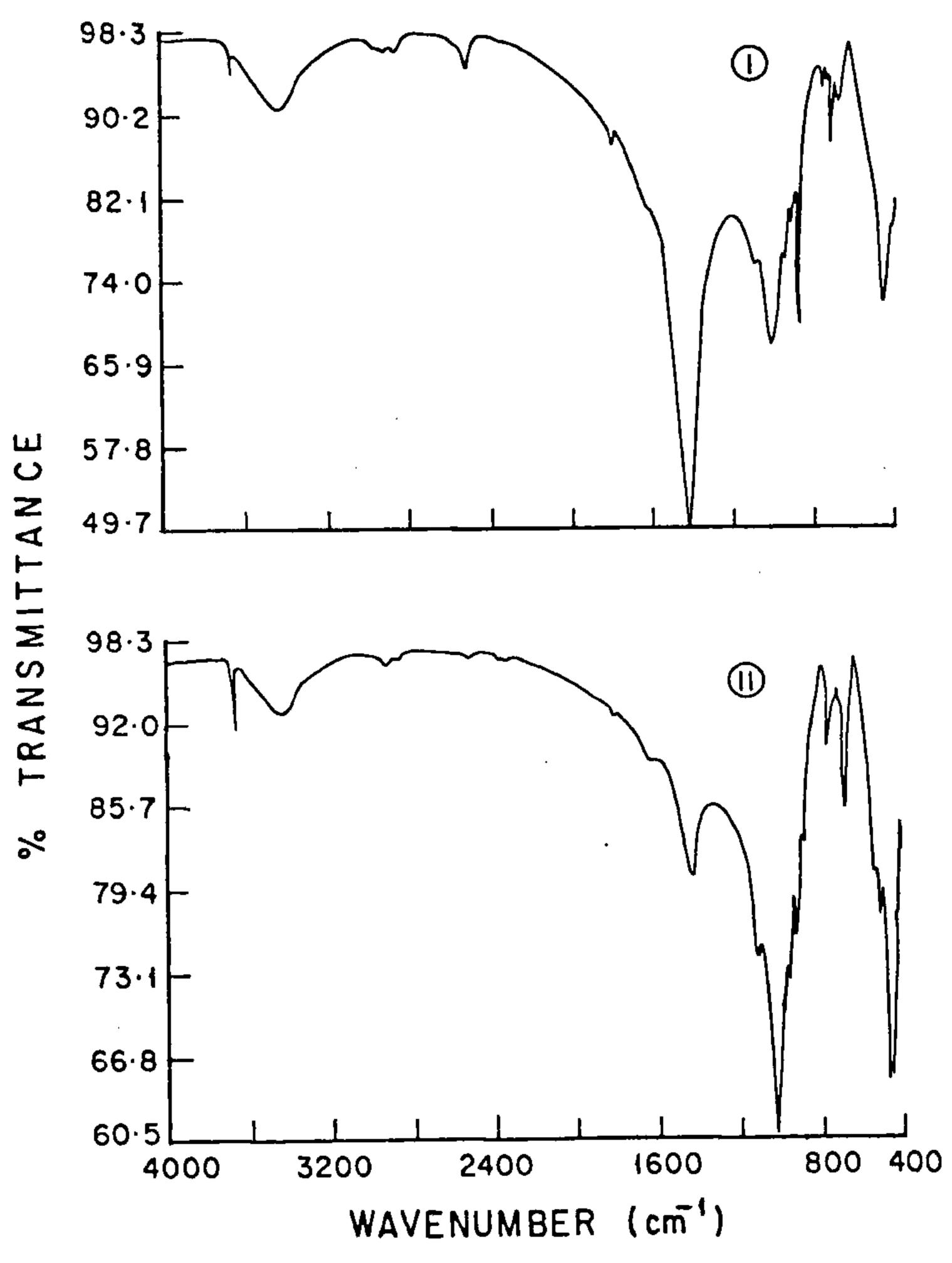


Figure 2. FTIR spectra of natural tremolites in the range 400-4000 cm⁻¹.

was attributed to the situation where the 'A' site is empty, 'T' is mainly occupied by Si and M(1) to M(3) by Mg ions⁵. In view of earlier studies by Hawthorne¹, the other weaker band observed around 3659 cm⁻¹ in both the samples could mainly be attributed to the partial occupancy of the M(3) site by Fe ions, while the shoulder band around 3693 cm⁻¹ could be due to the partial occupancy of the A site by Na and K ions. This shoulder band is clearly seen in sample II, though the total of Na and K is less than that of sample I and this could be due to the stronger amphibole-like band (around 3674 cm⁻¹) than the pyroxene-like band (around 3400 cm⁻¹).

From Figure 3 it is clear that a main broad band exists at around 3437 and 3430 cm⁻¹, respectively, for these two samples. Usually hydroxyl groups involved in a stronger hydrogen bonding scheme would absorb infrared radiation in that region. To the best of our knowledge such a band was not observed previously in natural tremolites. However, there are some reports¹⁸ dealing with the alteration of pyroxenes into tale and amphiboles, where the pyroxene-like band at lower wave numbers (i.e. 3450 cm⁻¹) coexists with that of the amphibole-like band at around 3645 cm⁻¹. In a detailed

study¹⁸ on diopside of metamorphic origin from Rajasthan (same location as that of sample I), it was established that the pyroxene-like band decreases at 800°C and 2 kbar pressure and the amphibole-like band rapidly increases with the addition of HCl¹⁸. These studies indicate that the alteration of pyroxenes into amphiboles occurs at some favourable hydrothermal environment with a specific pH value. On the other hand, transmission electron microscopy studies¹⁹ showed that the tremolites decompose into clino-pyroxenes at about 740°C. The coexistence of both amphibole- and pyroxenelike bands in (OH) stretching mode region in samples I and II indicates the presence of two types of hydroxyl groups, namely one with a weaker hydrogen bonding (amphibole-like) and another with a stronger hydrogen bonding (pyroxene-like). In other words, the crystallographic arrangement of hydroxyl groups would have undergone modifications. However, precise reasons for these modifications are not clear to us but the associated regional metamorphic events could be a plausible source. Further, observed anomalies in EPR spectra of these samples (described in the following paragraphs) also demand a detailed work on a wide number of samples of the region to understand regional metamorphism.

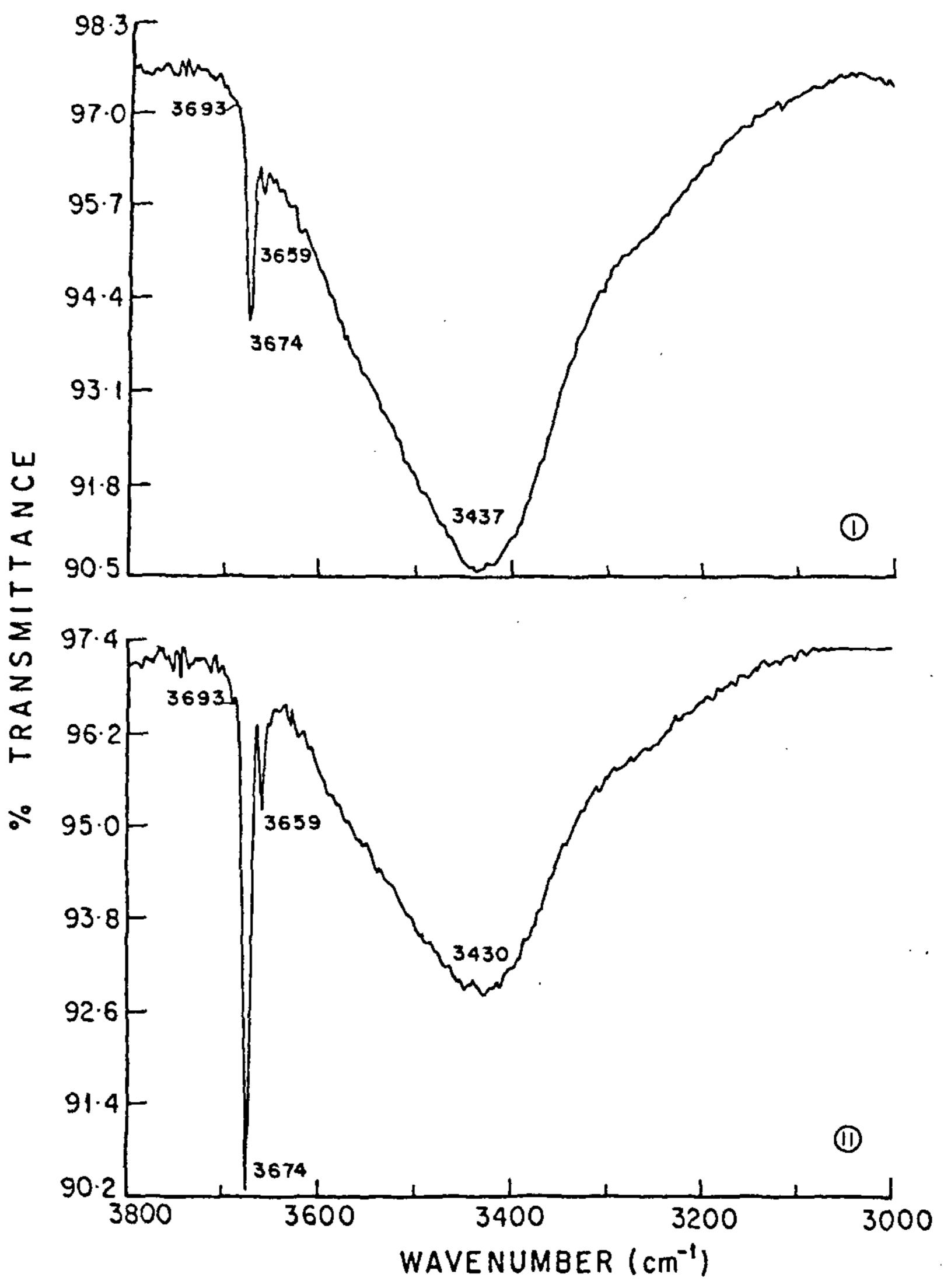


Figure 3. FTIR spectra of natural tremolites in (OH) stretching mode region.

The EPR spectrum of Mn^{2+} in natural tremolites was well studied. All the five groups of fine structural lines with a selection rule $\Delta M_s = \pm 1$ were found in single crystals in the X-band region along with the principal axes. Further, each group split into six components $(\Delta M_1 = 0)$ showing the hyperfine structure. These fine and hyperfine structures were observed to be well separated and resolved along two principal directions (a and c) while the lines were highly overlapped in another direction (b). Many forbidden lines with $\Delta M_1 = \pm 1$ were also observed in directions other than the principal axes. Thus in powdered or randomly oriented crystals one expects to observe the forbidden lines along with the allowed hyperfine lines.

The EPR spectra of samples I and II recorded at ambient conditions are shown in Figure 4 and they reveal

the existence of Mn^{2+} hyperfine lines along with many forbidden lines. It is also interesting to note that the allowed lines further split into two components on rotating the sample. This indicates that the Mn^{2+} ions occupy the interstitial M_4 site which is mainly populated by Ca ions. Further, the intensity of the hyperfine lines was gradually diminishing and the separation was increasing, a behaviour which was not observed previously in tremolites. The intensity variations of hyperfine lines could be attributed to the distortions within the crystallographic environment 20,21 . The intensity ratio of forbidden to allowed lines is an experimentally measurable quantity and this could be used to estimate the crystal field distortion parameter D, using the following relation⁹,

$$(I_f/I_a) = [(8D \sin 2\theta)/(g\beta B)] [(35/4) - m^2 + m],$$

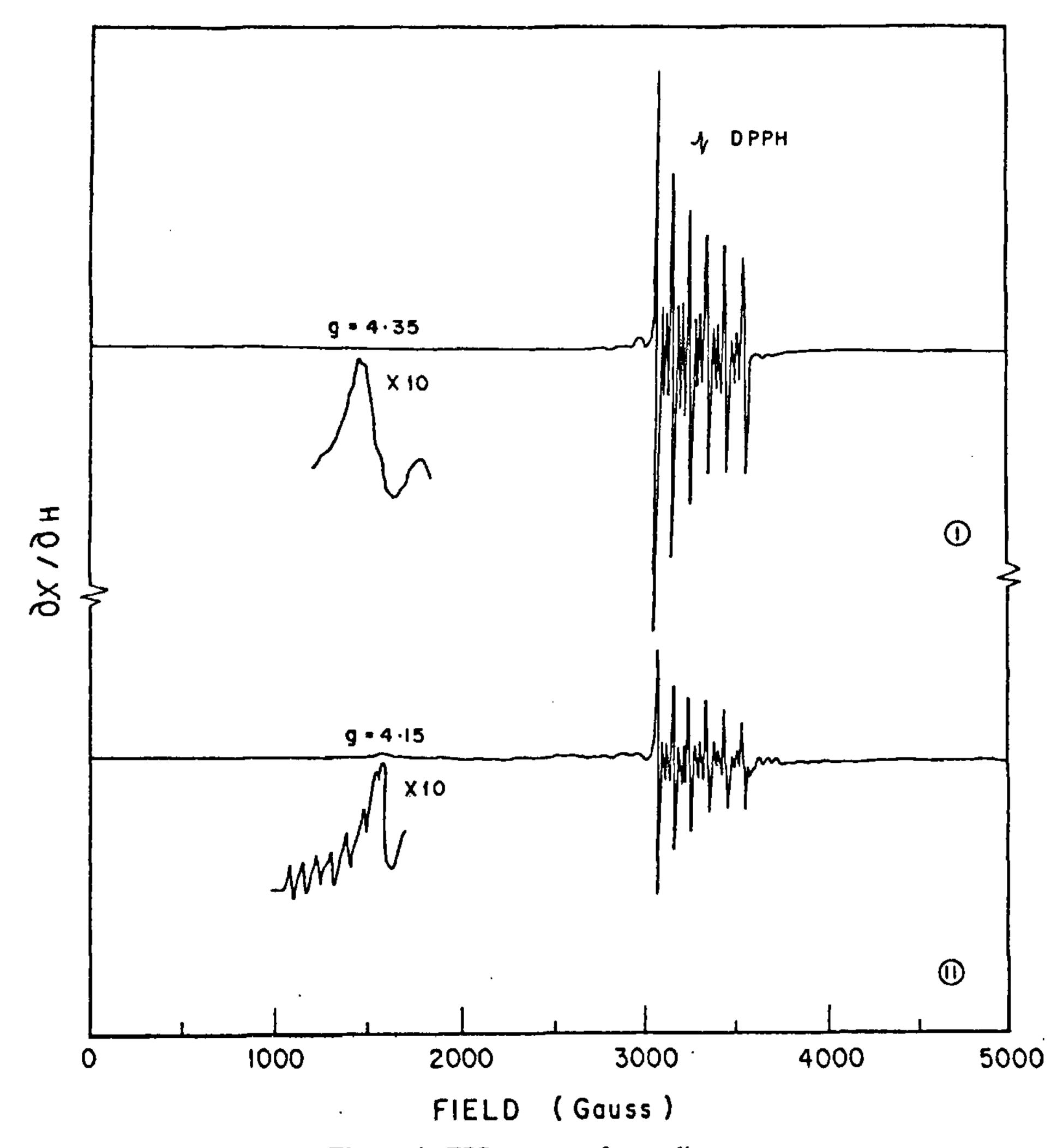


Figure 4. EPR spectra of tremolites.

where I_f and I_a are the intensities of the forbidden and allowed lines, respectively, and θ is the angle at which the magnetic field B is inclined to the crystal field.

For powdered samples the $\langle \sin 2\theta \rangle^2$ value could be replaced²¹ by (8/15). The ratio of (I_f/I_a) was around 0.2 for samples I and II, using which the value of D was estimated as $(8.5 \pm 2.0) \times 10^{-3}$ cm⁻¹ and $(9.20 \pm 2.0) \times 10^{-3}$ cm⁻¹, respectively.

Another independent way of estimating D is from the separation of allowed resonance peaks⁴. However, this consists of the terms with 'D' and 'A' and therefore can be used only with a complete knowledge of these hyperfine constants⁴. Nevertheless, we can use this for a very rough estimation of D. To a first-order approximation this separation is proportional to (D^2) (refs 4,9). The observed separation of allowed hyperfine lines in both the samples, was 7, 10, 10, 12, 15, 20 and 7, 9, 11, 14, 18, 22 G, respectively. The first-order approximation estimate of D from these separations resulted in a higher value compared to the one estimated from intensity ratios. These preliminary observations clearly indicate that the tremolites would have undergone some

distortions that may be typical of the distinctive geological episodes of the regions. However, further detailed symbiotic spectroscopic studies on more samples would certainly contribute towards a better understanding of metamorphic events of the region, which we plan to undertake in future.

The Fe ion could exist in both the oxidation states, namely Fe²⁺ and Fe³⁺. The Fe³⁺ ion is EPR active as this has unpaired electrons. There are very few EPR reports^{11,12} in the literature which show the presence of Fe³⁺ in tremolite. We observed a sharp resonance line around 1530 G of ferric ions in both the samples with an effective g_{eff} value of 4.35 and 4.15, respectively. From Figure 4 it is clear that no new resonant lines were observed even at a lower temperature (77 K). However, others¹² have observed at least three lines in the direction (B||y) and attributed it to the population on different sites. From our observation we conclude that the sites of Fe³⁺ may have equivalent crystallographic environment. Further studies are needed because of the complexity¹² associated with the Fe ions. This geff value is in close agreement with the value reported for Fe3+ ion in a completely rhombic crystal field.

To summarize, two continental amphiboles from different geological locations, were characterized to be tremolites. Coexistence of amphibole- (3674 cm^{-1}) and pyroxene- (3430 cm^{-1}) like bands in hydroxyl stretching mode region in FTIR indicates that the tremolites have undergone some structural modifications. From the anomalies in the hyperfine structure of EPR spectra, the field distortion parameter D was estimated to be $(8.5 \pm 2.0) \times 10^{-3} \text{ cm}^{-1}$ and $(9.2 \pm 2.0) \times 10^{-3} \text{ cm}^{-1}$, respectively. The isotropic behaviour of Fe resonance lines in both the samples indicates that it is located on an equivalent site of Mg in this tremolite. All these observations indicate that the tremolites have undergone some structural modifications plausibly due to the metamorphic events associated with the regions.

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Seismogenesis and deformation in the Deccan Volcanic province, Peninsular India

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Fault stability margin (SM) due to Deccan Trap overburden estimated for limiting boundary conditions and pore pressures that are not lithostatic is highest along the western pericontinental belt of active rifts (BARS) (h = 1.5 km, SM ~ 146 bars). Despite maximum strengthening of weak faults, the frequency of earthquakes is the highest in the BARS. Seismogenesis in the BARS is, therefore, attributed to augmentation of compressive stresses, though erosion and isostatic uplift may play a subordinate role in the southern part. The SM for pore pressures that totally cancel the normal stress is zero but it is suggested that such conditions may be rare where the hypocentres are shallow and the weak faults are possibly open to the surface.

The strain rates for events of $M \ge 4.0$ and/or $I \ge 5$ in the time span 1750–1997 AD (247 years) are the highest for the Kutch seismic domain, being 3.5 ×10⁻⁸/yr. They are similar for the BARS and SONATA belt being $1.2-1.5 \times 10^{-11}/\text{yr}$, and are lower by an order of magnitude $(1.7-4.2\times10^{-11}/\text{yr})$ in the Godavari and Saurashtra domains which have a more closely comparable continental crustal structure. The moment rate tensors estimated for BARS indicate the dominance of N-S compressional stresses. In view of preferred N-S orientation of BARS, we tend to believe that ridge push forces along the mid-Indian Ocean ridges may have a dominant contribution to the stress field of this region matching the Himalayan back thrust. The difference in moment release pattern between the BARS and the SONATA belt is probably due to the contrasting deep continental structure of these regions. The uncertainties in estimation of seismic moments, particularly for historical events, and other assumptions render the above conclusions tentative. However, differences of one or two orders of magnitude in strain rates and concordance of observations with geological and stress field measurements enhance their credibility.

THIS paper addresses three aspects of the seismicity of the Deccan Volcanic Province (DVP): (a) The effect of Deccan basalt cover on strengthening weak faults in the Precambrian basement; (b) The scalar moment release and strain rates in the different crustal provinces within the DVP, and comparison of the same with one of the

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