

## Dehydration and phase transformation in chrysotile asbestos—A radial distribution analysis study

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**Abstract.** Radial distribution analysis of x-ray intensities diffracted by chrysotile samples untreated and treated at different temperatures upto 900°C has been carried out. Interatomic distances, coordination numbers, mean square displacements and the interatomic coupling constants for different pairs of atoms have been calculated from the radial distribution curves. The interatomic distances and octahedral co-ordination number is found to decrease marginally upto 640°C and thereafter decrease steadily upto 800°C. The hydroxyl water is completely expelled from the structure and the original chrysotile structure breaks down. The entire process of dehydration has been interpreted in terms of RDF data.

**Keywords.** Dehydration; phase transformation; chrysotile asbestos; radial distribution.

### 1. Introduction

Chrysotile asbestos is of great scientific interest and commercial value because of its complexity of structure and multiplicity of uses. It belongs to the serpentine group of clay minerals with 1:1 layers which curl into cylindrical rolls. Its ideal structural formula is  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$  for half a unit cell. It is built up of alternate half layers of silicate and brucite. Misfit between the two results in curvature with the longer brucite layer lying on the convex side. The curved layers form cylindrical fibrils with the *a*-axis along the fibre axis, *b* along the circumference and *c* along the radius of the fibres (Brindley and Brown 1980). The crystal chemical state of water in this mineral can be classified into two distinct groups characterized by hygroscopic (or adsorbed) and hydroxyl according to their nature and location in the structure. It is well established that these water molecules play a dominant role at different stages of dehydration resulting in significant transformation of structural and physical properties (Datta *et al* 1986; Datta and Bhattacharjee 1986).

The dehydration transformation mechanism in chrysotile has been studied by various workers using the usual x-ray powder diffraction method supported by IR and TEM studies (Hey and Bannister 1948; Brindley and Zussman 1957; Martin 1977; Santos and Yada 1979; Glasser *et al* 1962). Broadly, the results of these works show that chrysotile with loss of structural water transforms into an anhydride phase around 600°C followed by the formation of forsterite. Finally above 800°C the anhydrous phase recrystallizes into enstatite. However, the exact nature of the entire sequence of this transformation mechanism is yet to be fully understood.

From the review of literature, it is clear that notwithstanding the industrial potential and geochemical importance of this mineral, its x-ray crystallography and structure remain disputed till date owing to nonavailability of single crystal of

suitable size. The problem is further complicated by the poorly crystalline form of this mineral which produces ill-defined powder patterns marked by large number of overlapping diffused broad lines rendering the application of usual powder method difficult for structural study. The problem becomes still more acute in the case of dehydration products which are still less crystalline with higher concentration of disorders. Because of these facts the problem is still open and calls for a better approach for investigating the structural details, especially in these poorly crystalline transient products from their x-ray diffraction patterns. To a large extent most of the difficulties encountered in the analysis of these types of poorly crystalline materials can be surmounted by adopting the technique of radial distribution analysis which is considered to be one of the most powerful and suitable tools for the study of less crystalline, amorphous and highly disordered systems (Leonard 1977; Lokanatha *et al* 1984, 1985). This approach is relatively new for clay minerals. In recent decades several workers (Leonard 1977; Lokanatha *et al* 1984, 1985; De *et al* 1986) have applied this technique successfully for structural analysis of several clay minerals and their poorly crystalline dehydration products. They have been able to explain the transformation mechanism in a much better way compared to any existing standard methods. Hence in the present work this technique has been applied to study the transformation process in a sample of chrysotile.

## 2. Experimental methods

### 2.1 Sample preparation

A sample of chrysotile from Cuddapah was selected for the present investigation. For testing the purity and identification of the sample, chemical and x-ray analyses were carried out and the results have been reported earlier (Datta *et al* 1986). Chemical analysis revealed the presence of  $Al_2O_3$ , FeO and  $TiO_2$  in traces besides the principal constituents  $SiO_2$  and MgO. X-ray analysis showed the traces of quartz. The sample was finely powdered and sieved through a 325 mesh screen. Then it was divided into several parts and heated separately for 5 hr each at temperatures 580, 640, 700, 750, 800 and 900°C respectively. Heated samples were then cooled in a desiccator to avoid the absorption of moisture and rehydration.

### 2.2 Determination of intensities and radial distribution function

The sample preparation for recording diffraction patterns was similar to that described by Mitra and Bhattacharjee (1969). Recording of intensities in the angular range  $4^\circ$  to  $120^\circ$  ( $2\theta$ ) and subsequent corrections for different factors were carried out as described by Lokanatha *et al* (1985). Following the same procedure as outlined by these authors, the corrected intensities were scaled to electron units. Finally the radial distribution function (RDF) for a polyatomic system was obtained by using the equation

$$4\pi r^2 \rho_e(r) = 4\pi r^2 \rho_{oe} + (2r/\pi) \int_0^\infty Si(S)M_1(S)M_2(S)M_3(S) \sin rS dS,$$

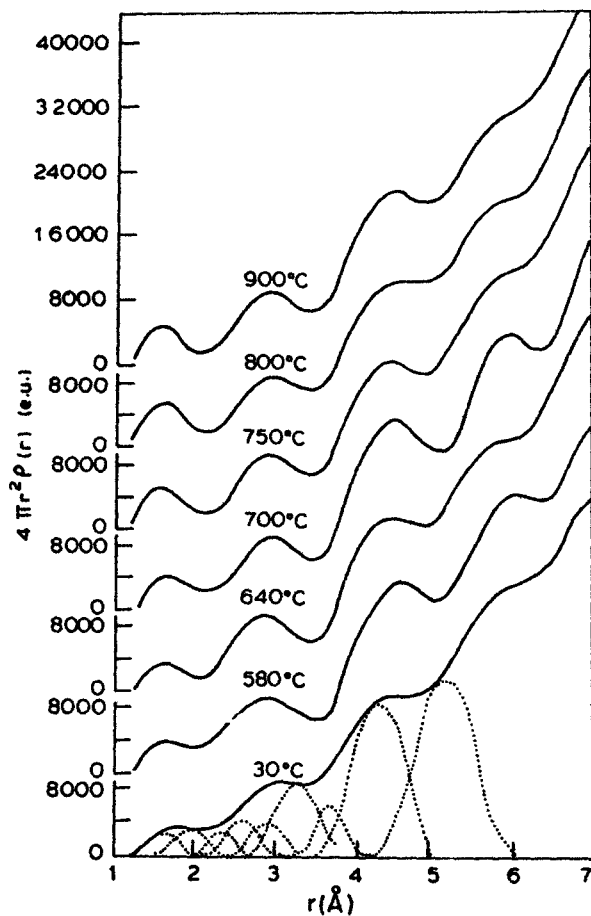
where the symbols have usual meanings (Lokanatha *et al* 1985).

In the present case, the value of the damping factor  $b$  was adjusted till the ripples in the low angle region were considerably reduced. After several trials an optimum value of  $b=0.001 \text{ \AA}^2$  was assumed. The RDF obtained from Fourier inversion curves, representing the intensity distribution in reciprocal space using the above equation, shows peaks at radial distances corresponding to different nearest neighbour positions. Some of the overlapped peaks have been resolved by fitting Gaussian profiles to individual peaks. The coupling constants associated with various interatomic distances of untreated as well as dehydrated products were calculated following the procedure of Kaplow *et al* (1968) to obtain an approximate idea of the relative strength of the bonds. The values of coordination numbers with dehydration for the first three nearest neighbours have been calculated by measuring the area under the peaks of the untreated and treated chrysotile sample at different temperatures.

### 3. Results and discussion

The RDF curves for untreated and treated samples at different temperatures are shown in figure 1. Results of the calculations made from RDF curves are shown in tables 1 to 3. It is observed that the first peak occurs at  $r=1.61 \text{ \AA}$  which corresponds to Si-O bond distance as reported in literature. It is interesting to note that unlike Lokanatha *et al* (1984, 1985) who observed the Si-O bond distances in fibrous silicate minerals to be much higher than the usual value as reported by Smith (1954), the present value is much closer to the value generally considered to be standard. Comparing this result with that of Lokanatha *et al* (1984, 1985), we conclude that substitution of Si, by trivalent ions which is attributed to the observed higher values in fibrous palygorskite and sepiolite, is less in chrysotile sample. The coordination number calculated from the area under the peak is 3.92 ( $\sim 4$ ) which confirms the tetrahedral coordination of silicon atoms as expected. Hence, the first peak can be associated with the tetrahedral group forming Si-O network in silicate minerals. The coordination number remains practically unaltered with marginal changes at 640°C and 800°C establishing the stability of silicate layer. This observation is in conformity with the stepwise transformations in chrysotile fibres leading to the formation of forsterite and enstatite as revealed by x-ray, DTA and IR studies (Datta *et al* 1986). As reported by Datta *et al* (1986), the first stage extends upto about 640°C when dehydration starts with the expulsion of hydroxyl water. Beyond 750°C, there is a rapid recrystallization to forsterite and enstatite. The marginal increase in the value of the coordination number in two successive steps at 640°C and 750°C respectively is certainly associated with the formation of new phases and indicates a better coordination in these new crystalline phases. The near constancy of the Si-O bond distance and coordination number reaffirms the earlier observations made by Brindley (1980) that the Si-O bonds and consequently the tetrahedral silicate layer are more stable than the metal oxygen parts forming the octahedral groups and maintain the structural continuity of the different phases with the parent matter and do not collapse even at high temperatures.

The second and the third peaks can be similarly associated with Mg-O bonds forming octahedral groups with values 1.98 Å and 2.33 Å and coordination numbers 5.5 and 5.4 respectively. These values of the Mg-O bond distances and their coordination numbers are slightly less than the standard values. These marginal deviations



**Figure 1.** Radial distribution function curves for untreated and treated chrysotile at different temperatures. For the sake of clarity, the origins of the successive curves have been shifted by 10000 e.u. along the ordinate.

**Table 1.** Variation of interatomic distances (Å) of chrysotile sample with dehydration.

Peak Number	Interatomic distances (Å)						
	30°C	580°C	640°C	700°C	750°C	800°C	900°C
Si-O	1.61	1.61	1.60	1.60	1.60	1.60	1.60
Mg-O <sub>I</sub>	1.98	1.97	1.96	1.96	1.95	1.95	1.95
Mg-O <sub>II</sub>	2.32	2.32	2.30	2.18	2.20	2.34	2.20
O-O	2.61	2.60	2.58	2.59	2.61	2.61	2.62
O-O	2.95	2.90	2.92	2.94	2.94	2.94	2.98
Si-Si	3.34	3.34	3.35	3.32	3.36	3.37	3.38
Mg-Si	3.70	3.74	3.72	3.66	3.70	3.73	3.74
Mg-Si	4.34	4.32	4.30	4.30	4.32	4.32	4.31
Si-Si	5.18	5.18	5.18	5.18	5.18	5.19	5.20

**Table 2.** Variation of the coordination numbers with dehydration for the first three neighbours.

Peak Number	Coordination numbers						
	30°C	580°C	640°C	700°C	750°C	800°C	900°C
Si-O	3.92	3.92	3.94	3.94	3.94	3.96	3.96
Mg-O <sub>I</sub>	5.50	5.40	5.30	4.90	4.40	4.40	4.60
Mg-O <sub>II</sub>	5.40	5.40	5.30	4.90	4.70	4.60	4.70

of bond distances and coordination numbers can very well be ascribed to the presence of vacancies in the octahedral sites which are invariably present and are greater in this type of trioctahedral silicate minerals. These vacancies are likely to upset the equilibrium of the bond forces resulting in this deviation from theoretically expected values which is necessary to adjust the octahedral coordination to a stable configuration. All other peaks listed in table 1 have been resolved and identified by comparing with the standard interatomic distances reported by Sueno *et al* (1973).

Unlike Si-O distances, most of the remaining interatomic distances, in general, are observed to decrease only marginally and irregularly with gradual dehydration upto 640°C. However, above this temperature the changes become appreciable in a few cases, especially the Mg-O distance at 700°C. These initial marginal variations which are most likely due to expulsion of some adsorbed water, are of no consequence from structural point of view.

It is observed from table 1 that different bond lengths in the present sample do not vary regularly by any appreciable amount with dehydration which starts actually from around 568°C and continues slowly upto 768°C as revealed by the DTA curve (Datta *et al* 1986). These variations of bond lengths may be considered to be insignificant for all practical purposes. Thus we can say that the structure remains almost stable even upto 640°C because of this slow rate of dehydration as was observed by Martin (1977). The minor changes at 640°C is obviously due to the commencement of loss of structural water. Below 640°C the sample consists primarily of chrysotile and hence this particular feature can be attributed to chrysotile alone. Hereafter, forsterite starts developing slowly followed by the rapid formation of enstatite at 800°C and above. Hence above 640°C the entire diffraction pattern considered for calculation of RDF, is due to the contribution of an admixture of anhydrous or amorphous chrysotile, crystalline forsterite and enstatite. However, the relative abundance of the different constituents will depend on the temperature above 600°C. The existence of this multiphase system above 600°C or so is borne out by x-ray and DTA observations (Datta *et al* 1986) and renders the analysis very difficult. Hence above 600°C, whatever values of the lattice parameters are obtained, should preferably be considered as a weighted statistical average which is averaged over all the three phases and their relative proportions. However, since the conversion rate is rather slow at the initial stage, we can quite justifiably consider the main constituent to be chrysotile and hence the parameters obtained also related primarily to this mineral below 700°C.

It is interesting to note that even at 700°C almost all the interatomic distances may be considered to remain more or less the same for all practical purposes barring however Mg-O<sub>II</sub> distances which change significantly. This drastic change in the

Table 3. Variation of the coupling constants and root mean square displacement of the chrysotile sample with dehydration.

Peak Number	Coupling constant (c.c) and r.m.s displacement ( $\langle u^2 \rangle^{\frac{1}{2}}$ ) in Å											
	30°C	580°C	640°C	700°C	750°C	800°C	900°C	c.c.	$\langle u^2 \rangle^{\frac{1}{2}}$	c.c.	$\langle u^2 \rangle^{\frac{1}{2}}$	
Si-O	0.405	0.28	0.374	0.27	0.374	0.27	0.366	0.26	0.376	0.26	0.371	0.26
Mg-O <sub>I</sub>	0.550	0.38	0.513	0.37	0.499	0.36	0.535	0.38	0.579	0.40	0.599	0.42
Mg-O <sub>II</sub>	0.507	0.35	0.458	0.33	0.458	0.33	0.450	0.32	0.521	0.36	0.514	0.36
O-O	0.666	0.46	0.624	0.45	0.597	0.43	0.605	0.43	0.623	0.43	0.585	0.41
O-O	0.666	0.46	0.611	0.44	0.583	0.42	0.591	0.42	0.608	0.42	0.628	0.44
Si-Si	0.608	0.42	0.569	0.41	0.583	0.42	0.591	0.42	0.608	0.42	0.599	0.42
Mg-Si	0.811	0.56	0.794	0.54	0.708	0.51	0.718	0.51	0.739	0.51	0.728	0.51
Mg-Si	1.0	0.69	1.0	0.72	1.0	0.72	1.0	0.71	1.0	0.69	1.0	0.70
Si-Si	0.797	0.55	0.805	0.58	0.777	0.56	0.746	0.53	0.768	0.53	0.771	0.54

value of interatomic distance between the farthest oxygen from Mg atom occupying the octahedral layer, primarily in the dehydrated chrysotile, leads to the collapse of chrysotile structure. The process is followed by simultaneous conversion of a major fraction to amorphous state and a minor fraction into crystalline forsterite. This observation on instability of structural organization of Mg is in agreement with the results obtained by Lokanatha *et al* (1984, 1985) and several other earlier workers. Increase of all the interatomic distances above 700°C clearly demonstrates the formation of the crystalline forsterite followed by forsterite and enstatite both at the final stage.

Table 2 shows that Si-O coordination number remains constant till 750°C and from 800°C there is an increase in the same. This is obviously due to the formation of crystalline enstatite which also results in sharpening of electron density function. This is also supported by the fact that the x-ray diffraction patterns of the sample heated at this temperature exhibit prominent peaks of enstatite corresponding to  $d=2.91, 2.55, 2.31$  Å respectively along with the peaks of forsterite and chrysotile (Datta *et al* 1986). The DTA curve also showed an exothermal peak at the same temperature indicating recrystallization of the sample. It is observed that the octahedral coordination number decreases marginally, like the interatomic distances upto 640°C with dehydration; thereafter changes steadily and attains the minimum average value of about 4.5 around 800°C. This clearly demonstrates that all hydroxyl water is completely expelled from the structure at 800°C as is evidenced from the DTA curve. The original chrysotile structure breaks down and a part of it subsequently recrystallizes, in addition to forsterite, into a crystalline enstatite whose yield proportion goes on increasing with temperature. Thus the disorder starts in the octahedrally coordinated magnesium atoms which are reorganized primarily into tetrahedral coordination as was observed in palygorskite and sepiolite by Lokanatha *et al* (1984, 1985). The slightly higher value compared to those reported in case of palygorskite and sepiolite may be attributed to the complex multiphase system existing in this temperature range in the present sample.

An attempt has been made to calculate the coupling constants and the root mean square displacements ( $\langle u^2 \rangle^{\frac{1}{2}}$ ) associated with the various interatomic distances of untreated as well as the dehydrated products following the methods of Morimoto (1958) and Kaplow (1972). The calculated values of  $\langle u^2 \rangle^{\frac{1}{2}}$  and the coupling constants tabulated in table 3 reveal that the strongest bondings are between Si-O, Mg-O and Si-Si. With an increase in temperature, there is no appreciable variation in the  $\langle u^2 \rangle^{\frac{1}{2}}$  values and consequently no significant change in the strength of the bonds even upto 640°C. This fact lends further support to our earlier observation that the structure remains stable upto this temperature without any significant disorder being introduced by dehydration. However, at higher temperatures,  $\langle u^2 \rangle^{\frac{1}{2}}$  values corresponding to Mg-O are found to increase and consequently the strength decreases. This is somewhat expected and is in conformity with other results. But the variations of  $\langle u^2 \rangle^{\frac{1}{2}}$  values for other atom pairs are too insignificant to draw any definite conclusion on the structure except that the couplings of these atom pairs remain more or less unchanged in the new phases developed at temperatures above 700°C.

#### 4. Conclusion

The results of RDF analysis of the observed diffraction pattern enable us to arrive at

certain valuable conclusions on the structural reorganization of atoms in the different stages of thermal treatment of chrysotile samples. It is clear that upto about 600°C there is no significant change and only above 700°C, significant changes occur owing to the completion of dehydration and subsequent development of the various phases. These observations agree well with the results of DTA, IR, TEM and x-ray studies (Datta et al 1986).

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