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Local ordering structure of meta-kaolinite and meta-dickite by the X-ray radial distribution function analysis

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X-ray diffraction measurements on the structure of meta-kaolinite and meta-dickite have been carried out to obtain the radial distribution function(RDF). The distances and corresponding coordination numbers for Si–O and Al–O pairs were estimated by applying the pair function method. The SiO_4 tetrahedron remains unchanged in the dehydrated samples presently investigated, and the oxygen coordination number around aluminium was also found to be four. This implies the overall preference of AlO_4 tetrahedron at the expense of the parent $AlO_2(OH)_4$ octahedron.

1. Introduction

The series of reactions by which kaolinite transforms to mullite has been recognized as one of the most important subject areas in ceramic technology. Thermal treatment of kaolinite up to 1600 K induces various atomic rearrangements. The previous results on differential thermal analysis (DTA) shows an extensive endothermic peak at about 830 K and two exothermic peaks at about 1250 and 1450 K, respectively. The endothermic peak around 830 K is known to be caused by dehydration and is closely related to the meta-kaolinite formation. The origin of the former exothermic peak at 1250 K has been attributed to the formation of γ-Al_2O_3 and/or crystalline mullite, although the latter exothermic peak is generally considered to be the crystallization of mullite and cristobalite (e.g. [1]).

Meta-kaolinite has been suggested to have, at least, some residual structure relevant to kaolinite, in which the Si–O tetrahedral sheets of kaolinite are almost unchanged when the dehydration reaction occurs, even though the three-dimensional regularity disappears [2, 3]. The environmental structural change around aluminium induced by dehydration has been studied by various methods, such as X-ray fluorescence analysis [4–6], X-ray diffraction [7, 8], infrared spectroscopy [6, 9, 10], and recently nuclear magnetic resonance using magic angle spinning (MAS/NMR) [11–13]. Thus four-fold coordination of aluminium at the expense of six-fold coordination is suggested in the structure of dehydrated kaolinite and dickite. With these facts, various structural models of meta-kaolinite and related structures have been proposed by introducing the four-fold coordination of aluminium and silicon coupled with the parent kaolinite structure [2, 3, 7, 12]. On the other hand, a new concept for the structure of meta-kaolinite has recently been proposed based on the results of the high-resolution MAS/NMR measurements. In meta-kaolinite samples, the signal for a silicon linked with four other silicons or aluminiums was detected at temperatures above 773 K (near the onset temperature of dehydration). This suggests the transformation of a two-dimensional sheet structure into a three-dimensional network structure by inducing the phase segregation of both silica and alumina. The five-fold aluminium with the usual four-fold one by dispensing with part of a six-fold aluminium, has also been proposed in meta-kaolinite structure [14–16], although this five-fold aluminium may be the product in the early or intermediate stage of the dehydration process [15].

The direct determination of the fundamental local ordering unit of meta-kaolinite and meta-dickite is essentially required for explaining these extensive results quantitatively. Although some X-ray structural data of meta-kaolinite or meta-dickite are available [7,8], they cannot explicitly elucidate the recent spectroscopic results. For this reason, the main purpose of this work was to present a new systematic structural investigation of meta-kaolinite and meta-dickite by the X-ray radial distribution function analysis.

2. Experimental procedure

Kaolinite sample was taken from commercial kaolinite powder (Ultra White 90, Engerhard Co. Ltd) and the dickite sample was prepared from dickite block from Syokozan Mine, Okayama Prefecture, Japan. To obtain the dickite sample, the original block was ground in a mechanical agate mortar for about 60 min, yielding a powdered sample of below 44 μm. The chemical composition was determined by X-ray fluorescence analysis and the results are shown in Table I. The preliminary X-ray diffraction (XRD)

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analyses of these parent materials were attributed to the results of JCPDS cards 14-164 (kaolinite) and 10–446 (dickite), although 0.7 mass % anatase appears to be included in the kaolinite sample. The dehydration reactions of these samples were carried out in an alumina crucible at temperatures of 900, 1000, 1100, 1200 and 1300 K for 60 min and the dehydrated products were cooled in air. A small amount of volatile elements, such as residual hydroxyl, was detected in the successive ignition loss tests for each sample as shown in Table II. The densities of the samples were measured by Archimedes' method with toluene.

XRD profiles for all samples were measured using MoK_α radiation with a singly-bent pyrolytic graphite monochromator in a diffracted beam in the wave-vector range of $Q = 5$–$150\ \mathrm{nm}^{-1}$. Here $Q = 4\pi \sin\theta/\lambda$, where θ is half the angle between the incident and diffracted beams, and λ is the wavelength of the incident beam. After applying corrections for absorption, polarization, and Compton scattering [17, 18] to the measured intensity data in the usual manner [19], the X-ray scattering intensities were converted into electron units, by the generalized Krogh–Moe–Norman method [20] with the density values, and then the reduced interference function $Qi(Q)$ was obtained. In this work, the observed intensity data at $Q < 5\ \mathrm{nm}^{-1}$ were smoothly extrapolated to zero at $Q = 0\ \mathrm{nm}^{-1}$. The effect of this extrapolation or truncation up to $Q = 150\ \mathrm{nm}^{-1}$ for the broad peaks observed in a disordered system is known to make no significant contribution to the radial distribution function (RDF) calculated from the interference function by the Fourier transformation [21].

TABLE I The chemical compositions (mass %) of kaolinite and dickite samples determined by X-ray fluorescence analysis

	Kaolinite Ultra White 90	Dickite Syokozan
SiO_2	47.22	47.41
Al_2O_3	36.19	37.61
Fe_2O_3	0.44	0.31
TiO_2	0.64	0.24
Na_2O	0.30	0.11
K_2O	0.04	n.d
CaO	0.04	0.08
MgO	0.01	n.d.[a]
Ig. loss	14.76	14.39

[a] n.d. = not detected.

3. Data processing

The method for analysing the X-ray diffraction patterns of disordered systems is very common and has already been described in detail [17–19]. Consequently, only the essential features are given below.

The electron RDF can be readily estimated by applying Fourier transformation to the interference function in electron units, $i(Q)$, which are defined as

$$i(Q) = [I_{\mathrm{eu}}(Q)/N - \sum_{\mathrm{uc}} f_j^2]/f_\mathrm{e}^2 \qquad (1)$$

$$\mathrm{RDF}_{\mathrm{exp}} = 2\pi^2 r \rho_\mathrm{e} \sum_{\mathrm{uc}} Z_j + \int_0^{Q_{\max}} Qi(Q) \mathrm{e}^{-\alpha^2 Q^2} \sin Qr \, \mathrm{d}Q \qquad (2)$$

where I_{eu}/N is the intensity of unmodified scattering in electron units per unit of composition, f_j and f_e are the atomic scattering factor and the average scattering factor per electron, respectively. ρ_e is the average number density of electrons and Z_j is the atomic number of element-j. The amount of residual hydroxyl for each sample was estimated from the successive ignition loss values in Table II and it was included in the chemical composition of each sample for data processing. In the present case, the unit of composition is considered to be composed of four major elements of silicon, aluminium, oxygen and hydrogen. The term of $\exp[-\alpha^2 Q^2]$ is a convergence factor, usually introduced to minimize the truncation error and weigh down the uncertainties at the higher wave-vector region. However, the value of α is assumed to be zero in the present calculation of the experimental RDF.

On the other hand, the electron RDF can also be calculated for particular distances r_{ij} and coordination numbers N_{ij} of i–j pairs using the pair function distribution (PFD) equation [22]

$$\mathrm{RDF}_{\mathrm{cal.}} = \sum_{\mathrm{uc}} \sum_{i} \frac{N_{ij}}{r_{ij}} \int_0^{Q_{\max}} \frac{f_i f_j}{f_\mathrm{e} f_\mathrm{e}} e^{-\alpha^2 Q^2} \sin Qr_{ij} \sin Qr \, \mathrm{d}Q \qquad (3)$$

TABLE II The distances and coordination numbers estimated by the pair function method along with ignition loss and measured density values of meta-kaolinite and meta-dickite.

	Temp. (K)	Si–O		Al–O		O–O		Ig. loss[a] (mass %)	Density (Mg m^{-3})
		(nm)	(atom)	(nm)	(atom)	(nm)	(atom)		
Kaolinite	900	0.161	4.0	0.178	4.0	0.268	6.1	1.3	2.45
	1000	0.162	4.0	0.178	4.0	0.268	6.1	1.2	2.47
	1100	0.161	4.0	0.178	4.0	0.267	6.1	0.4	2.50
	1200	0.161	4.0	0.179	4.0	0.267	6.2	0.4	2.50
Dickite	900	0.162	4.0	0.178	4.0	0.265	6.1	1.6	2.44
	1000	0.162	4.0	0.178	4.0	0.266	6.0	1.4	2.46
	1100	0.162	4.0	0.178	4.0	0.266	6.0	0.2	2.50
	1200	0.162	4.0	0.178	4.0	0.268	6.1	0.3	2.50

[a] Ignition loss was measured at 1373 K.

The correlation distance is readily determined from the position of the corresponding peak in the experimental RDF data. In addition, the coordination numbers can be estimated by finding the quantity of N_{ij} which will bring the calculated RDF using Equation 3 to the best fit with the experimental RDF. In this process, the value of $\alpha = 0.06$–0.09 is employed on the basis of previous studies on various oxide glasses [23]. In this process, the variation of r_{ij} and N_{ij} in experimental RDF are ± 0.002 nm and ± 0.2 atom, respectively. It may be worth mentioning that the data processing using Equation 3 is effective only for a few near-neighbour correlations.

4. Results and discussion

Fig. 1a and b show the X-ray diffraction profiles of meta-kaolinite and meta-dickite samples. The small spikes of (0 0 2) and (0 0 4) Bragg reflections remain in dickite heated at 900 K, although such incidental observation vanishes on dehydration at higher temperature. The very small amount of impurity originated from other crystalline components, such as anatase in the case of kaolinite, appeared to be isolated from the halo patterns and were smoothly eliminated from the major diffraction profiles. It may be noted that such elimination is insignificant to the calculation of RDF. The basic features of these diffraction profiles are no closer to the original kaolinite and dickite structure than the common disordered structure like silicate glasses. It may also be added that several small spikes were again detected at $Q = 11, 18, 23, 26, 32, 41$ and $45\ \text{nm}^{-1}$ in samples heated at 1300 K, and crystallization to form $\gamma - Al_2O_3$ and mullite in these samples has been detected, by matching the spike positions with the JCPDS cards 10–425 and 15–776, respectively. Therefore, the RDF analysis of the dehydrated samples at temperatures of 900, 1000, 1100 and 1200 K were made together with the procedure given in Section 3. It is worth mentioning that the scattering intensities in the low Q region indicating structural inhomogeneity is appreciable, particularly in meta-kaolinite and meta-dickite samples dehydrated at temperatures of 900, 1000 and 1100 K. This might be related to the breakdown of the parent structure of kaolinite or dickite by the occurrence of heterogeneous contraction [24, 25], although no definite comment on this problem can be given and it is out of the scope of the present work.

Fig. 2a and b show the reduced interference functions $Qi(Q)$ of the meta-kaolinite and meta-dickite samples. The general features of the reduced interference functions $Qi(Q)$ for all samples are similar to those of typical oxide glasses. Namely, the profiles of $Qi(Q)$ are composed of the first peak at about $Q = 16\ \text{nm}^{-1}$ followed by a number of peaks, which contrast with the cases of metallic glasses where the damping behaviour of the function $Qi(Q)$ is rapid and monotonic [18]. If species having definite bond lengths and angles exist, persistence of the oscillation in $Qi(Q)$ would be clearly detected in the high Q region [20]. Therefore, the oscillations observed in these metaphases imply that a considerable fraction of the local ordering unit structure remains, although its distribution appears to be random. The SiO_4 tetrahedra are quite feasible with respect to the local ordering unit structure in these samples which are given below.

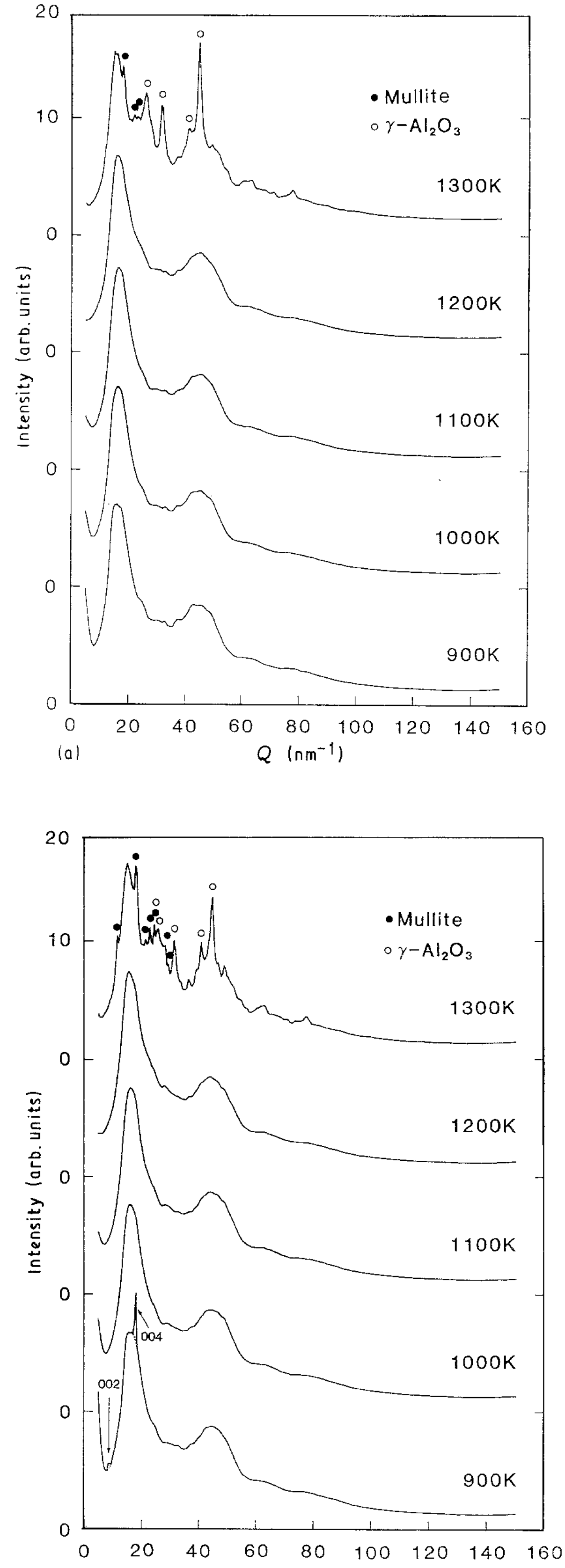

Figure 1 X-ray diffraction profiles for the dehydrated (a) kaolinite and (b) dickite samples as a function of heating temperature obtained by MoK_α radiation. The sharp Bragg reflections in dickite heated at 900 K are smoothly eliminated from the major diffraction profiles as shown by dots.

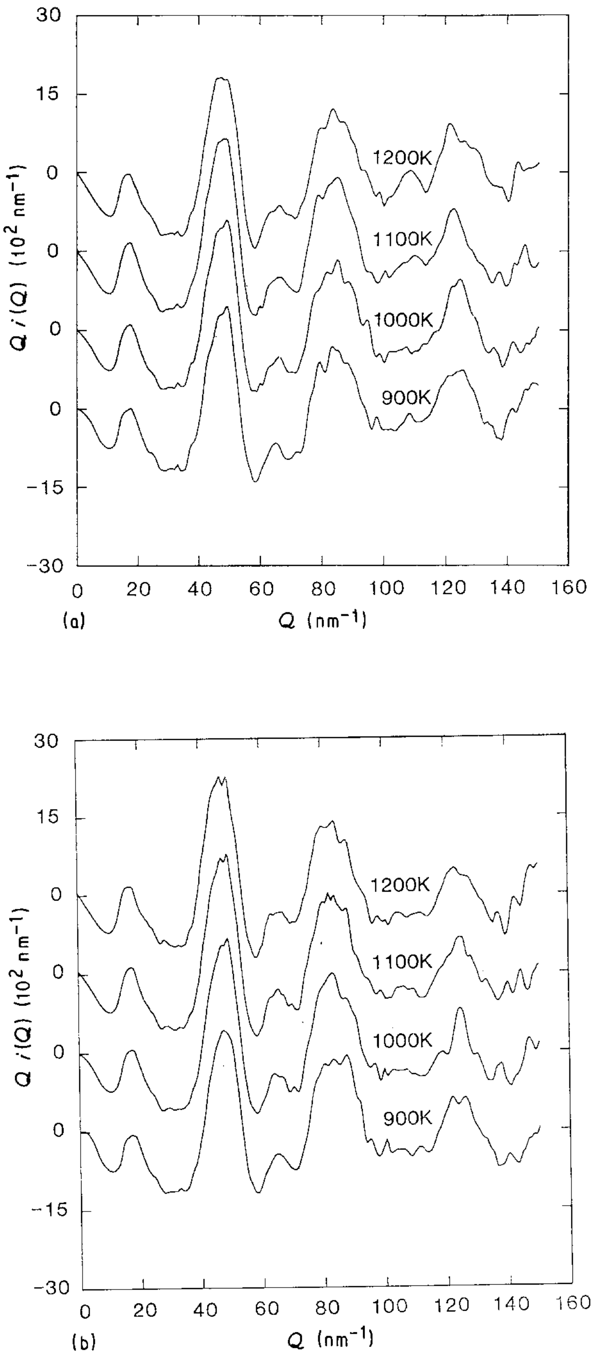

Figure 2 Reduced interference function of Qi (Q) for the dehydrated (a) kaolinite and (b) dickite samples as a function of heating temperature.

The RDFs of meta-kaolinite and meta-dickite samples are shown in Fig. 3a and b, which correspond to the Fourier transformation of the $Qi(Q)$ functions in Fig. 2a and b, respectively. The general feature of the RDFs is again found to be almost independent of the dehydration temperature. The first peak at around 0.17 nm in the RDFs of all samples appears almost completely resolved and the subsequent oscillations are reduced so as to converge to the average number-density value at the larger distance of r. Information of such local ordering unit structures could be obtained by fitting the respective peaks with the pair function method. The oscillations of RDF in the small r region before the first peak are not sufficiently reduced, although the origin of such oscillations cannot be identified with certainty at the present time. It is also added that such oscillations are also suggested to have no critical effect on the evaluation of interatomic distances and coordination numbers [21].

Crystalline kaolinite and dickite are known to have the two-layered unit structure where an octahedrally coordinated aluminium sheet is linked with a tetrahedrally coordinated silicon sheet. Each silicon shares three oxygens with three silicon tetrahedra and one oxygen with two octahedral aluminium. An aluminium is coordinated to two oxygens of the tetrahedral sheet and to four hydroxyl groups. For convenience of discussing the structural features of meta-kaolinite and meta-dickite, several interatomic distances in crystalline kaolinite and dickite are calculated and their averaged values are shown by arrows in Fig. 3a and b, respectively [26]. Taking into account these atomic pairs of crystalline kaolinite and dickite, it is probably reasonable to identify the first peak at around 0.17 nm with a harmony of Si–O and Al–O contributions, and the second one around 0.27 nm with O–O pairs. The peak around 0.32 nm corresponds to the mixed correlation of several atomic pairs such as Si–Si, Si–Al and Al–Al pairs. Therefore, the interatomic distances and coordination numbers of the first three correlations were estimated by the pair function method. The results are summarized in Table II. The calculated RDFs with the structural parameters listed in Table II are given using the results of samples heated at 900 K as an example. The results lead to the following remarks.

The resolution of the first peak in the RDF for both kaolinite and dickite samples is insufficient to separate the two peaks of Si–O and Al–O pairs. However, the most feasible values with physical meaning for oxygen coordination number around silicon or aluminium were obtained in this work by reproducing the experimental data using the PDF equation. The number of oxygens around silicon in the present dehydrated samples is estimated to be four. Thus, the SiO_4 tetrahedra remain unchanged as the local ordering unit structures in these samples, while the coordination number of Al–O pairs is also found to be four. This implies that the dehydration reaction induces a change in the local ordering around aluminium from $AlO_2(OH)_4$ to AlO_4. The present X-ray diffraction results could not provide definite information on the fraction of four- and six-fold aluminiums in meta-kaolinite and meta-dickite as proposed from the MAS/NMR measurements [14–16]. A large number of aluminiums in meta-phases are likely to be distributed in distorted sites which correspond to neither truly octahedral nor tetrahedral positions and this might be readily attributed to very broad and weak NMR signals, close to the limit for detection [12, 13]. Therefore, the four-fold coordination of aluminium is suggested in the present dehydrated samples, at least in the sense of a necessary condition for reproducing the X-ray diffraction results. It may be added that the estimated interatomic distance for Al–O pairs is 0.18 nm, which agrees with that of 0.176 nm in sillimanite (Al_2SiO_5) structure [27]. The present structural information concerning aluminium does not allow the remaining characteristics of the parent structure, as

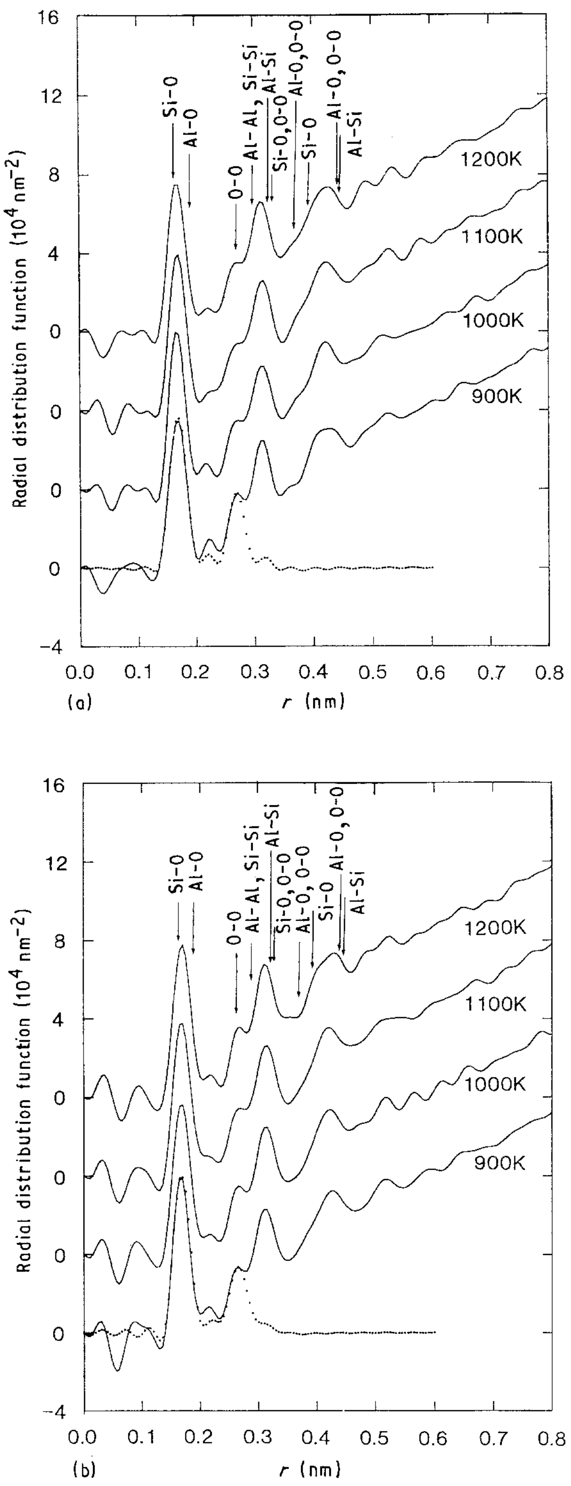

Figure 3 Electron radial distribution functions (RDFs) for the dehydrated (a) kaolinite and (b) dickite samples as a function of heating temperature. (—) Experimental data and (···) an example of the calculated sum of a few pair functions. The arrows indicate positions of some pairs observed in kaolinite and dickite [26].

suggested by Leonard [9], and rather appears to support the almost collapsed structure as predicted in recent MAS/NMR results [16–18]. With these facts in mind, meta-kaolinite and meta-dickite are likely to have several types of structure, such as a rather intact two-dimensional structure and an almost collapsed three-dimensional one, as suggested by Rocha and Klinowski [16]. This may also be due to the different dehydration reactions caused by the variation in grain size, crystallinity or heating conditions [1, 24].

The present RDF analysis for the dehydrated kaolinite and dickite samples suggests that the crystalline kaolinite or dickite structure is collapsed by dehydration and changes its structure towards disordered atomic arrangements, similar to those of silicate glasses. This includes the variation of the environmental structure around aluminium where aluminium of $AlO_4(OH)_2$ octahedra changes its coordination number into reduction. The present structural information is obviously insufficient to build up a full structural model of meta-kaolinite and meta-dickite. Nevertheless, we hold the view that the dehydration of crystalline kaolinite and dickite readily induces its structural breakdown. It would be useful to carry out some further diffraction experiments using neutron diffraction or energy-dispersive X-ray diffraction facilities in order to obtain more precise information about aluminium and its role in the dehydration process.

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