

## ON THE IDENTIFICATION OF THE MINERALS OF KAOLINITE SUBGROUP USING X-RAY POWDER METHOD

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**Abstract.** Because of the close resemblance of the X-ray powder patterns of the minerals of the kaolinite series, particularly kaolinite and dickite, it becomes difficult to differentiate one from the other using the ordinary X-ray powder method of identification. Based on the examination of a composite X-ray powder pattern of kaolinite and dickite, and supported by other evidences based on the analysis of some specific lines, a procedure has been worked out which would help in uniquely identifying the two minerals, even with the usual cameras which have rather poor resolution.

The minerals of the kaolinite subgroup, namely kaolinite, dickite, and nacrite are chemically and structurally very closely related: they are all basic silicates of aluminium having the chemical formula  $Al_4(Si_4O_{10})(OH)_8$ . The space lattice of kaolinite has invariably been described as monoclinic,<sup>1-4</sup> while a number of investigators have proposed triclinic space lattice for kaolinite. There is little confusion as regards dickite and nacrite: they form monoclinic space lattice. The space lattice of kaolinite, however, has been controversial. On the one hand there appears to be such a close correspondence in the X-ray powder patterns (taken with 11.4 cm diameter camera) of kaolinite and dickite that one would be very much inclined to believe that kaolinite has the same space lattice as that of dickite (i.e. monoclinic), but on the other hand Brindley et al.<sup>5</sup> very strongly advocate that the space lattice of kaolinite is triclinic rather than monoclinic, their argument being that the reflexions cannot be indexed with Gruner's<sup>6-7</sup> monoclinic cell. On closer examination of Brindley's indexing, however, one observes that all the reflexions (even the probable alternative indices corresponding to the same  $d$ -values) satisfy the following conditions:

The general  $h k l$  reflexions, are present only for those values of  $h$  and  $k$  for which  $h + k = 2n$ , suggesting that the  $C$ -face is centred.

Significantly enough there is not one single exception, and one would wonder if they could still be regarded as purely accidental absences. It may, therefore, be that the absences are real and thus the space lattice proposed by Gruner for kaolinite cannot be discarded altogether.

However, perhaps the latest studies by electron diffraction<sup>8</sup> provide somewhat assuring evidence for the space lattice of kaolinite to be triclinic, yet the triclinic cell dimensions ( $a = 8.89$  kx,  $b = 5.13$  kx,  $c = 7.25$  kx,  $\alpha = 104^\circ 40'$ ,  $\beta = 91^\circ 40'$ ,  $\gamma = 90^\circ$ ) are so close to the monoclinic cell, except for the  $c$ -axial length, that for practical purposes it would not be an unreasonable simplification to index the kaolinite pattern on the basis of a cell formed by taking two units of triclinic cell along the  $c$ -axis which would, in effect, correspond with Gruner's monoclinic cell. Based on this cell the corresponding reflexions of kaolinite and dickite would have more or less the same

indices. The cell dimensions of the three minerals are given in Table 1.

As can be seen from the data given in Table 1, the X-ray powder pattern of nacrite should be sufficiently different from those of kaolinite and dickite, and there should not be much difficulty in uniquely identifying it from the other members of the series using X-ray powder methods. But kaolinite and dickite present difficulties, for their cell parameters are closely comparable, so that the  $d$ -values of their powder patterns would be so close as to warrant special precautions in measurements in order to differentiate between them. Even the intensities of the corresponding lines would not be very different because the two structures are also very closely comparable.

In view of the foregoing, it occurred worthwhile to look into this problem and to work out some methods of identifying the two minerals from one another using their X-ray powder patterns taken with cameras of moderate resolution which are normally used for identification purposes.

### Analysis of the Problem

In order to compare the differences in  $d$ -values of the corresponding lines on the two patterns (i.e. the lines having the same  $h k l$  indices) the analytical expression for  $d^*$  may be examined for the triclinic cell.

$$d^{*2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2 h l a^* c^* \cos \beta^* + 2 h k a^* b^* \cos \alpha^* + 2 k l b^* c^* \cos \alpha^*.$$

As the axial lengths of the two cells are very close (using the double cell for kaolinite), the differences in the  $d^*$ -values of kaolinite and dickite pattern may be approximated, for any reflexion  $h k l$ , by

$$\Delta^2 \simeq d_{kt}^{*2} - d_{Dt}^{*2} \simeq 2 h l a^* c^* (\cos \beta_{kt}^* - \cos \beta_{Dt}^*) + 2 k l b^* c^* (\cos \alpha_{kt}^* - \cos \alpha_{Dt}^*),$$

where  $d_{kt}^* = d^*$  kaolinite,  $d_{Dt}^* = d^*$  dickite

In general  $\Delta^2$  will be small. It may, however, become significantly large for some values of  $h k l$ . The expression can be rewritten as follows:

$$h l = \frac{\Delta^2}{2 a^* c^* (\cos \beta_{kt}^* - \cos \beta_{Dt}^*) + 2 k / h b^* c^* (\cos \alpha_{kt}^* - \cos \alpha_{Dt}^*)}$$

In general the value of  $hl$  depends both on  $h$  as well as  $k$  but because  $a^*c^*(\cos\beta_{KT}^* - \cos\beta_{DT}^*)$  is about eight times larger than  $b^*c^*(\cos\alpha_{KT}^* - \cos\alpha_{DT}^*)$  and as the maximum magnitude of  $k/h$  for strong reflexions is two, the term  $b^*c^*(\cos\alpha_{KT}^* - \cos\alpha_{DT}^*)$  may be neglected. Thus

$$hl \simeq \frac{\Delta^2}{2a^*c^*(\cos\beta_{KT}^* - \cos\beta_{DT}^*)}$$

As  $a^* = 0.195\text{\AA}^{-1}$ ,  $c^* = 0.069\text{\AA}^{-1}$  the value of  $hl$

for 1% difference in  $d$ -values at  $d = 2.0\text{\AA}$  will be given by

$$hl \simeq \frac{0.005}{2 \times 0.195 \times 0.069 \times 0.133} \simeq 1.4$$

As the value of  $hl$  should be 1.4 at the limit of resolution, the actual reflexions that can be seen to be resolved will, in general, be the ones for which  $hl$  is equal to or greater than 2, for  $hl$  can only have integral

values. It must be emphasised that because  $\delta\cos\beta^*$  is sufficiently large near  $\beta^* \simeq \pi/2$  it is essential to have accurate values of  $\beta^*$  for the two structures. If the monoclinic cell data for kaolinite is adopted, the value of  $hl$  works out to 3. After all these are simply limiting values and serve only as guides for picking up the reflexions which may show up the difference in  $d$ -values more prominently, and as such the lower value of the two may be adopted. Thus the corresponding lines on the patterns of kaolinite and dickite, the  $hkl$  indices of which are such that the product  $hl$  is equal to or greater than 2, will have more than 1% difference in their  $d$ -values at  $d = 2.0\text{\AA}$ .

With any powder camera, the accuracy in the measurements of  $d$ -values increase with the angle  $\theta$ . With a 11.46 cm dia powder camera, the overall expected accuracy, in the middle angular range of the camera, is of the order of 1%. Thus it would appear that for any significant differences in the corresponding  $d$ -values of the two patterns in the middle  $\theta$  range of the camera, one should look for reflexions having

TABLE 1

Mineral	Lattice type	$a$	$b$	$\alpha$	$\beta$	$\gamma$
Kaolinite	triclinic†	5.14A°	8.91A°	7.26A°	91°40'	104°40'
	monoclinic‡	5.14A°	8.90A°	14.45A°	90°	100°12'
Dickite	monoclinic‡	5.14A°	8.94A°	14.42A°	90°	96°50'
Nacrite	monoclinic‡	5.15A°	8.931A°	28.66A°	90°	91°43'

†data taken from Zuyagin's paper<sup>8</sup>,  $a$  and  $b$  have been interchanged to conform to the cell dimensions of dickite.

‡data taken from Betekhtin's book on mineralogy.<sup>1</sup>

Note: More accurate cell dimensions for dickite and nacrite have been worked out by later workers, but there is no controversy about their space groups.

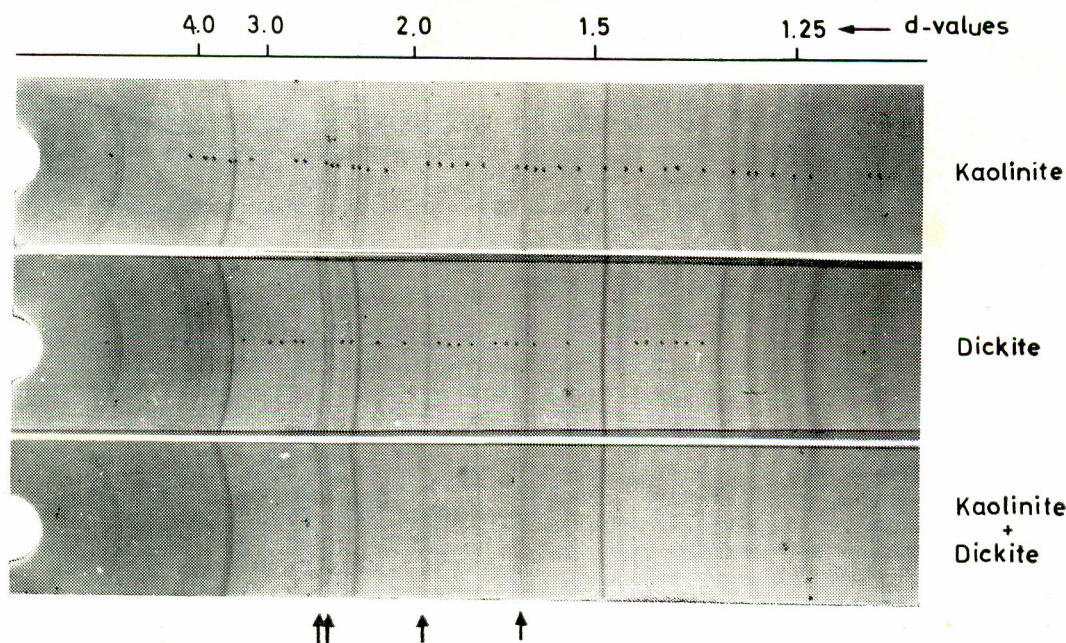


Fig. 1. X-ray powder photographs of kaolinite, dickite, and 1:1 mixture of kaolinite and dickite.

TABLE 2

<i>d</i> -values of kaolinite, from ASTM card (with intensities)	Index according to triclinic cell	Re-indexing of distinguishing lines based on the doubled cell	Product $ hkl $ for the distinguishing lines	
Region A				1.616 (70) $24\bar{2}, 310, 15\bar{1}$
7.15 (100)	0 0 1			$133, 24\bar{2}$
4.45 (50)	0 2 0			1.581 (40) $15\bar{2}, 13\bar{4}$
4.35 (60)	1 $\bar{1}$ 0			1.539 (60) $241, 22\bar{4}, 11\bar{4}$
4.17 (60)	1 1 $\bar{1}$			$13\bar{4}, 31\bar{3}, 20\bar{3}$
4.12 (30)	1 $\bar{1}$ $\bar{1}$			Region C
3.84 (40)	0 2 $\bar{1}$			1.486 (90) $060, 33\bar{1}$
3.73 (20)	0 2 1			1.464 (10) $06\bar{1}, 33\bar{2}, 22\bar{3}$
3.57 (100)	0 0 2			1.262 (30) $26\bar{2}, 33\bar{4}$
3.37 (40)	1 1 1			$15\bar{4}$
3.14 (20)	1 1 $\bar{2}$			
3.09 (20)	1 $\bar{1}$ $\bar{2}$			
Region B				
2.75 (20)	0 2 2			
*2.55 (70)	$1\bar{3}0, 20\bar{1}, 130$	$1\bar{3}0, 20\bar{2}, 130$	0, 4, 0	
2.52 (40)	$13\bar{1}, 1\bar{1}\bar{2}$			
*2.486 (80)	$1\bar{3}1, 200, 11\bar{2}$	$1\bar{3}\bar{2}, 200, 11\bar{4}$	2, 0, 4	
2.374 (70)	0 0 3			
2.331 (90)	$20\bar{2}, 1\bar{3}\bar{1}$			
2.284 (80)	$1\bar{1}\bar{3}, 1\bar{3}\bar{1}$			
2.243 (5)	$13\bar{2}, 040$			
2.182 (30)	$201, 1\bar{3}\bar{2}, 2\bar{2}0$			
2.127 (20)	$023, 041$			
2.057 (5)	$023, 2\bar{2}\bar{2}$			
*1.985 (70)	$20\bar{3}, 1\bar{3}\bar{2}$	$20\bar{6}, 1\bar{3}\bar{4}$	12, 4	
1.935 (40)	$221, 132$			
1.892 (20)	$113, 1\bar{3}\bar{3}$			
1.865 (5)	0 4 2			
1.835 (40)	$1\bar{3}\bar{3}, 20\bar{2}, 22\bar{3}$			
1.805 (5)	$11\bar{4}, 2\bar{2}\bar{3}$			
1.778 (60)	0 0 4			
1.704 (5)	2 $\bar{2}$ 0			
1.682 (10)	$1\bar{5}0, 2\bar{4}\bar{1}, 3\bar{1}\bar{1}$			
	$3\bar{1}\bar{1}, 2\bar{2}\bar{2}$			
*1.659 (80)	$2\bar{4}0, 20\bar{4}, 15\bar{1}$			
	$2\bar{4}0, 20\bar{8}, 15\bar{2}$	$1\bar{3}\bar{6}$	0, 16, 2, 6	
	$13\bar{3}$			

These data on kaolinite have been taken from A.S.T.M. Card index (1955 edition), which are based on the work of Brindley *et al.* The *c*-axis based on Brindley's cell is half that of Gruner's. As such on the basis of Gruner's data, the indices of the reflexions can be obtained by doubling the value of *l*, as given in Brindley's data.

the indices such that the product *hl* may be sufficiently larger than 2. An examination of the powder data of kaolinite (Table 2) shows that, with Cr-radiation, the reflexions appearing in the middle  $\theta$  range will have indices such that  $hl \geq 2$ . Using shorter radiations will only coverage the significantly strong lines to comparatively very low  $\theta$  angle where the resolution will be much poorer.

It does appear that in the middle angular range of the camera, using Cr-radiation, there would occur some reasonably strong reflexions for which the corresponding *d*-values of the lines on the two patterns would differ by 1% or more. Although independent measurements of individual patterns as such may not provide convincing evidence to consider such differences significant, yet one would expect that if a composite pattern be taken of a mixture of kaolinite and dickite one might observe broadening of some of the lines due to slight differences in their *d*-values. One may even predict these lines, for these must be the ones for which the product *hl* should generally be greater than 2. Thus an experimental method of identification suggests itself.

#### Experimental

X-ray powder patterns of some standard samples of kaolinite and dickite were taken. Cr-radiation was used, for this naturally gives better resolution of the diffraction lines. The two patterns are shown in Figure 1 along with a pattern of a mixture of the two minerals in 1 : 1 ratio.

As expected, some of the lines corresponded to *d*-values of 2.55, 2.49, 1.985, 1.659, (marked  $\uparrow$ ) do appear to be broadened. These lines are shown in Table 2 by (\*) mark. The diffractometric traces corresponding to the three patterns reproduced in Fig. 1 were also taken and are given in Fig. 2. The broadening of the peaks corresponding to the four lines indicated in Fig. 1 are indicated in Fig. 2 by arrow marks. Even in Fig. 2 one can see an unmistakably clear evidence of line-broadening of some specific lines in the pattern of the 1 : 1 mixture sample.

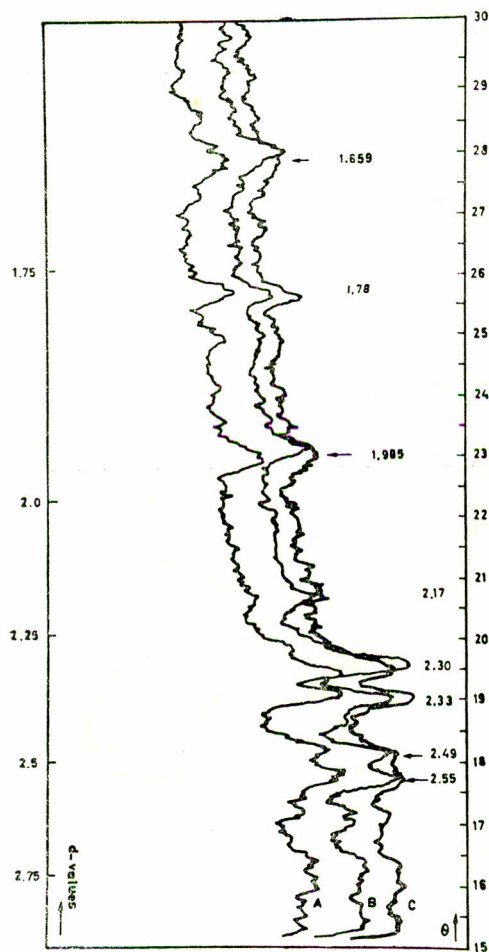


Fig. 2. Diffractometric trace of the diffraction lines of kaolinite (curve A) dickite (curve B) and 1:1 mixture (curve C)

Thus if one had an unknown sample to be tested for the presence of kaolinite or dickite one could identify it by examining three X-ray powder patterns, one corresponding to the sample as such, the second of a 1:1 mixture of the sample with standard kaolinite, and the third of a 1:1 mixture of the sample with standard dickite. Only one of the two patterns of composite sample would show the broadening of the specific lines mentioned above. The sample corresponding to this pattern will suggest that the sample itself does not contain the phase with which it has been mixed, and thus will provide the evidence for the presence of the other alternative.

There may, however, be some difficulties in a straight forward application of this method. As the intensities of the four specific lines are in the medium strong range they may not be so clearly visible in the pattern of a sample containing the minerals only as a minor component. In such cases a systematic examination of the pattern may be undertaken and even other evidences may be looked for.

#### Results and Discussions

It has been seen that in a sample containing one of these minerals as a major component an examination of the powder pattern of two mixtures of the

sample, one with standard kaolinite and the other with standard dickite, may help to uniquely identify the mineral. In any case, however, further supporting evidence may also be looked for. Some of the high angle lines may, indeed, be useful in this respect. In Table 2 the standard data of kaolinite is reproduced from the ASTM<sup>9</sup> data card.

Using Cr-radiation one does obtain a couple of reflexions of medium intensities in the high  $\theta$  range having the product  $hI \geq 2$ . These reflexions will evidently appear to be very much out of step with each other on the two patterns of kaolinite and dickite, and if they do appear, then the magnitudes of the  $d$ -values themselves will characterise the pattern which will provide a useful supporting evidence.

Thus the whole procedure of identification may be summarised as follows:

- Cr-radiation should preferably be used for taking the photographs
- The entire pattern may conveniently be divided into three regions in accordance with the expected resolution of the lines in these regions. A convenient division has been shown in Table 2.
- In the middle region of the pattern the evidence for the broadening of the lines may be examined as outlined in the foregoing.
- Some of the lines in the high angle region (Fig. 1) particularly the lines corresponding to  $d$ -values less than or equal to 1.35 may be examined. The accuracy of measurements for these lines will be sufficient to identify whether they belong to the kaolinite or the dickite pattern. A comparison of the two patterns would show that the lines are significantly out of step in this region. This can be clearly seen in Fig. 1 as well. It may, however, be further emphasised that these medium strong lines will appear in the high angle region only if the radiation used is of larger wavelength which further brings out the case for using Cr-radiation.

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