EFFECTS OF GRINDING ON DICKITE

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ABSTRACT

Data are presented for the effects of wet and dry grinding on dickite from Ouray, Colorado. With increase in dry grinding time the endothermic d.t.a. peak becomes broader and moves towards a lower temperature, while the exothermic reaction is greatly sharpened. Weight loss data, demonstrate greater water loss from ground material and over a longer temperature range. X-ray powder photographs show that after a relatively short period of grinding little further destruction of the lattice occurs, and this lattice destruction apparently proceeds only to a certain stage, for high order spacings of hk/l are very persistent.

INTRODUCTION

Attention has frequently been centred around the action of grinding on various minerals and chemical compounds, especially in the field of clays, and the effects on the base exchange properties of such minerals. Kelley, Jenny and Brown (1936), Perkins and Draggsdorf (1951), Jackson and Truog (1939), Mackenzie and Milne (1953). While the effects of prolonged grinding on kaolinite are well known Laws and Page (1946), Gregg, Parker and Stephens (1953), little work has been undertaken on two of the other members of the kaolinite group namely dickite and nacrite. From the evidence available it would seem that dickite behaves in a somewhat similar fashion to kaolinite Kelley, Jenny and Brown (1936), but a detailed investigation shows some pronounced differences.

The dickite selected for the experiments was that chosen by the American Petroleum Institute, Project 49 (1951) as a reference clay sample. Labelled No. 14 it is from South of Ouray on U.S. 550 (near Red Mountain pass) Colorado, U.S.A. The origin of this mineral and the associated mineralised areas of the Silverton caldera have been described by Burbank (1941). Specimens of this dickite are white in colour, powdery, and show good crystal outline. It was decided to experiment with material of a fixed grain-size distribution, and therefore the grain-size 20 microns to 2 microns was chosen (silt fraction) and separated—after preliminary hydrogen peroxide treatment—by centrifugal means from the finer fractions, and gravitational settling from the coarser fractions. Actually it was found that almost all the material fell within this grade, and therefore the material used in the experiments is very closely akin to the original specimen. Samples of the fraction were dry ground for periods of 2, 6, 15, 24, and 140 hours and one sample ground wet for 60 hours, in a mechanical pestle and mortar. The sample ground wet had a small amount of sodium metaphosphate added to aid dis-
The various ground fractions and unground material were investigated by differential thermal analysis, weight loss on dehydration, and X-ray powder photography.

**RESULTS**

The differential thermal curves are rather similar to those given by Laws and Page (1946) for ground kaolinite. These authors noted an endothermic reaction below 350°C which gradually became stronger, while the normal 500°C circa. reaction became weaker. The curves for dickite are presented in Fig. 1 where it will be seen that ostensibly the same effect is produced. The cause of the double endothermic peak in material ground dry for two hours (No. 2 Fig. 1) is probably due to differences in reactivity between ground and unground material. There is a marked difference between ground and unground material for the high temperature 980°C circa. exothermic peak. With grinding, even after two hours, the intensity of this peak is much stronger, due it would seem to an increase in amount of amorphous material. The reaction for some members, especially those ground for long periods of time, were so violent as to cause difficulty in obtaining them on the graph.

Because of the great reduction of the normal thermal reaction corresponding to loss of lattice water on the thermal analysis graphs, data on weight loss due to increased temperature are desirable. These were obtained by heating small amounts of the material for periods of 24 hours at the various temperatures indicated. It is realised that such measurements may not represent equilibrium conditions, but after 24 hours heating the figures must be very close to—if not identical with—equilibrium figures. The weight loss data have been compiled into a table (Table 1) and to permit more rapid scrutiny have been presented in graphical form in Fig. 2. The sudden explosion-like loss of water from the unground dickite in the 500°C region is well shown for the unground material. With increasing time of grinding the loss of water is shifted to a lower temperature and becomes more evenly distributed over a wider temperature range, but in all cases the loss does not cease until over 750°C circa. the decrease being much slower for the ground material. The graphs bring out quite clearly the pronounced changes which take place even with grinding for so little time as two hours. The changes which take place after 15 hours grinding are relatively small and it will be noted that the curve for material ground for 140 hours is not markedly different from that for material ground 15 hours; in fact they are for all practical purposes identical in the region above 500°C. The grinding took place with free access to the air and therefore, water has been absorbed from the atmosphere due to increase in surface-area, and total water contents are always greater for ground material. Again, very little change occurs after 15 hours grinding.

In the high temperature region there are decreases shown by downward flexures of the weight loss graphs. These flexures
Fig. 1—Differential thermal curves for dickites. 1—unground material; 2—ground 2 hours; 3—ground 6 hours; 4—ground 15 hours; 5—ground 24 hours; 6—ground 140 hours; 7—ground wet 60 hours.
<table>
<thead>
<tr>
<th>Dickite ground for</th>
<th>100</th>
<th>196</th>
<th>306</th>
<th>450</th>
<th>525</th>
<th>680</th>
<th>750</th>
<th>870</th>
<th>1050</th>
</tr>
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<tr>
<td>2 hours dry</td>
<td>1.74</td>
<td>4.35</td>
<td>5.72</td>
<td>13.18</td>
<td>16.16</td>
<td>17.04</td>
<td>17.16</td>
<td>15.42</td>
<td>15.67</td>
</tr>
<tr>
<td>6 ,, ,,</td>
<td>4.96</td>
<td>10.21</td>
<td>13.33</td>
<td>19.36</td>
<td>20.43</td>
<td>20.72</td>
<td>21.11</td>
<td>20.91</td>
<td>21.01</td>
</tr>
<tr>
<td>24 ,, ,,</td>
<td>5.57</td>
<td>13.24</td>
<td>17.03</td>
<td>21.15</td>
<td>21.79</td>
<td>22.20</td>
<td>22.44</td>
<td>22.44</td>
<td>22.44</td>
</tr>
<tr>
<td>140 ,, ,,</td>
<td>6.73</td>
<td>14.27</td>
<td>18.04</td>
<td>21.10</td>
<td>21.58</td>
<td>22.29</td>
<td>22.48</td>
<td>22.48</td>
<td>22.48</td>
</tr>
<tr>
<td>60 hours wet</td>
<td>3.99</td>
<td>8.20</td>
<td>9.92</td>
<td>17.15</td>
<td>18.23</td>
<td>18.88</td>
<td>19.42</td>
<td>19.31</td>
<td>19.42</td>
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<tr>
<td>unground</td>
<td>0</td>
<td>0.06</td>
<td>0.37</td>
<td>2.70</td>
<td>7.85</td>
<td>13.41</td>
<td>13.72</td>
<td>12.79</td>
<td>13.04</td>
</tr>
</tbody>
</table>
represent an increase in weight of the sample. The increase is greatest for material unground or ground for only a short period, and is absent after 15 hours or more grinding. The cause of this is probably oxidation of ferrous oxide to the ferric state. This oxide must be enclosed within the individual flakes of dickite for otherwise the

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**Fig. 2—Cumulative Percentage Weight Loss of Dickites Ground for varying times.**

- Unground Material
- Ground 2 Hours Dry
- Ground 6 Hours Dry
- Ground 60 Hours Wet
- Ground 15 Hours Dry
- Ground 24 Hours Dry
- Ground 140 Hours Dry

preliminary hydrogen peroxide treatment would have already oxidised the material. Furthermore after continued grinding the phenomenon decreases very rapidly, and after 6 hours, and certainly 15 hours, is zero. It seems quite likely that this is the explanation of
the phenomenon, for in the material analysed by the A.P.I. project (1951), ferous oxide was recorded.

One other feature which the curve brings out is the much greater efficiency of dry grinding over wet grinding, for it can be seen in the graphs that the material ground wet 60 hours lies intermediate in position between two hours and six hours dry grinding. It is fairly obvious therefore that very long periods of wet grinding would be needed to reach the equilibrium which is apparently obtained after 15 hours dry grinding.

The results of X-ray powder analysis are presented in Table 2. For the purpose of this table, only those lines which were observed in the ground samples have been recorded, in order to reduce an otherwise very cumbersome array of figures. For the unground and ground 2 hours material all powder lines occurred (66 measured), but after 2 hours grinding the number present decreases markedly. This effect is very noticeable after 6 hours grinding. Naturally, with increased grinding time the amount of amorphous material increases considerably, and the powder pattern lines become blurred due to distortion of the lattice. There is, however, an apparent anomaly here, for after 6 hours grinding the films become slightly clearer in the low angle end. A perusal of the data in Table 2 shows the great difference in effects between wet and dry grinding. Whereas dry grinding strongly distorts the lattice, wet grinding apparently causes shear along the perfect basal cleavages and therefore the values do not alter very considerably for 00l spacings (except 004). With dry ground material there is a steady increase in d for these spacings. For hkl spacings, again not much effect occurs for wet grinding, but dry grinding causes differences in d. The decrease in strength of 002 and 004 reflections with increase in grinding are interesting, in exhibiting successive destruction of the lattice. The change with 008 is nowhere nearly so marked.

The conclusions which may be reached from the evidence therefore would seem to point to the following. During dry grinding, the shearing stresses cause an expansion of the lattice in the Z direction and consequently the water escapes much more readily and at a lower temperature. The amount of increase in surface area should cause the amount of adsorbed water to rise sharply, and such is found to be the case. The decrease in some spacings may be related to the expansion along Z, but is more likely to be due merely to distortion of the crystals during grinding. From the evidence presented it seems that grinding is not efficacious after a certain fine grain size is reached, and therefore high index hkl lines should all still be present in ground material. If sufficient exposure time is given to the specimen ground 140 hours, such is found to be the case, but in such X-ray photographs there is no trace of low angle reflections due to low values of hkl.

Acknowledgements. I am indebted to The Trustees of the Leverhulme Research Fellowships for their financial support of this work and to Dr T. F. Bates of The Mineral Sciences Dept., Pennsylvania State College for the laboratory facilities he so generously placed at my disposal.
### Table 2—X-ray powder diagrams for ground and unground dickites

<table>
<thead>
<tr>
<th>Unground</th>
<th>Ground 60 hours wet</th>
<th>Ground 2 hours dry</th>
<th>Ground 6 hours dry</th>
<th>Ground 15 hours dry</th>
<th>Ground 24 hours dry</th>
<th>Ground 140 hours dry</th>
<th>Indices</th>
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<tbody>
<tr>
<td></td>
<td>$d$</td>
<td>I</td>
<td>$d$</td>
<td>I</td>
<td>$d$</td>
<td>I</td>
<td>$d$</td>
</tr>
<tr>
<td>7.151</td>
<td>vs</td>
<td>7.167</td>
<td>s</td>
<td>7.203</td>
<td>s</td>
<td>7.239</td>
<td>w</td>
</tr>
<tr>
<td>4.408</td>
<td>m</td>
<td>4.399</td>
<td>s</td>
<td>4.398</td>
<td>s</td>
<td>4.356</td>
<td>b</td>
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<tr>
<td>4.108</td>
<td>m</td>
<td>4.173</td>
<td>m</td>
<td>4.128</td>
<td>m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.576</td>
<td>vs</td>
<td>3.597</td>
<td>vs</td>
<td>3.595</td>
<td>vs</td>
<td>3.594</td>
<td>mw</td>
</tr>
<tr>
<td>3.330</td>
<td>w</td>
<td>3.364</td>
<td>m</td>
<td>3.351</td>
<td>m</td>
<td>3.357</td>
<td>m</td>
</tr>
<tr>
<td>2.504</td>
<td>m</td>
<td>2.524</td>
<td>m</td>
<td>2.506</td>
<td>m</td>
<td>2.542</td>
<td>vw</td>
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<tr>
<td>2.322</td>
<td>s</td>
<td>2.324</td>
<td>s</td>
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<td>vw</td>
</tr>
<tr>
<td>1.788</td>
<td>m</td>
<td>1.801</td>
<td>vw</td>
<td>1.793</td>
<td>w</td>
<td>1.820</td>
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<tr>
<td>1.556</td>
<td>m</td>
<td>1.558</td>
<td>m</td>
<td>1.557</td>
<td>m</td>
<td>1.541</td>
<td>vw</td>
</tr>
<tr>
<td>1.488</td>
<td>m</td>
<td>1.488</td>
<td>m</td>
<td>1.489</td>
<td>m</td>
<td>1.488</td>
<td>vw</td>
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<tr>
<td>1.374</td>
<td>w</td>
<td>1.378</td>
<td>b</td>
<td>1.375</td>
<td>w</td>
<td>1.375</td>
<td>vw</td>
</tr>
</tbody>
</table>

Measurements of $d$ in Å. $s =$ strong, $m =$ moderate, $w =$ weak, $v =$ very, $b =$ broad, $I =$ intensity
REFERENCES


DISCUSSION

Dr G. Nagelschmidt remarked that dickite was in reality more widespread than was generally recognised.

Dr McLaughlin initiated a discussion on the nature of the endothermic peak given by d.t.a. of dickite. His own curves and those shown by Mr G. Brown and Dr F. Smithson in the previous paper (published elsewhere) showed a pronounced tendency to give a shelf-like indentation which was quite different from the shelf sometimes observed in kaolinite. He reminded the meeting of Gruner's (1932) observations in which the conclusions were that from the evidence available two structural forms of dickite were possible, it being impossible to state which form was correct. McLaughlin suggested that the shelves were perhaps an indication of both forms co-existing. Nagelschmidt asked if any evidence of such a co-existence was forthcoming from other sources such as infra-red spectra. Dr R. C. Mackenzie in reply stated that only one peak could be observed in the infra-red, with no evidence of doubling.

Mr G. Brown questioned the validity of tracing the 008 spacing as spacings occurred at 1.790 and 1.788 (008 and 117). Dr H. P. Rooksby aligned himself with this view.

Dr McLaughlin stated that his reasons for ascribing the line observed to 008 were from the evidence of Fig. 2. The random shifts of spacings with grinding might well be expected to separate an overlapping hkl and 00l spacing. It did seem more reasonable to presume the line was 008 rather than 117, in view of the behaviour of other 00l spacings. Furthermore the intensities of 008 and 117 were different and Gruner had assigned the line to 008.

Dr Rooksby pointed out the difficulty of interpretation of dehydration data, for if γ-A12O3 formed only in the presence of water, then obviously some must be present even at quite elevated temperatures.

Mr A. N. Smith quoted experiments where adsorbed water was not lost until over 700°C in some clay minerals.

Dr S. J. Gregg enlarged on the difficulties involved in driving out the last traces of a volatile.

Dr McLaughlin pointed out that he had actually specified the fact that his results were non-equilibrium figures.
Dr Mackenzie commenting on the sharpening of the exothermic peak reported by McLaughlin, stated that the disorder introduced by grinding might be expected to produce a smaller peak.

Dr R. W. B. Nurse on this same point stated that nucleation proceeded faster with increase in surface. The specimens examined by McLaughlin were comparatively coarse (2-20μ) and the peak sharpening might perhaps pass through a maximum corresponding to a specific surface-area relationship.

Dr McLaughlin drew attention to the lattice distortion as evidenced by X-ray photographs and mere particle size reduction could not therefore be the full explanation of this rather puzzling phenomenon.