Note on the occurrence of anatase in some fireclay deposits.

By G. W. BRINDLEY, M.Sc., Ph.D., Reader in X-ray Physics,
and KEITH ROBINSON, Ph.D., Research Assistant,
Physics Laboratories, University of Leeds.

[Read November 6, 1947.]

IN X-ray studies of fireclays we have frequently observed the presence of anatase to the extent of 1 or 2 % with little or no rutile, and no brookite. Chemical analyses of these clays usually record 1–2 % of TiO_2 and occasionally more (Ennos and Scott, 1924). The mineralogical form of the TiO_2 is usually not stated, but a number of references to the observance of rutile needles give the impression that rutile is the form in which titania occurs in these deposits. Our own observations based on X-ray powder photographs lead us to conclude that anatase is commonly present and that rutile is either absent or present in smaller quantities. We have not detected brookite.

The presence of anatase in fireclays is easily revealed by X-ray powder photographs when a camera of adequate resolving power is employed (e.g. a 20-cm. diameter camera used with Cu-$K\alpha$ radiation). The strongest anatase line at 3·51 Å. is adjacent to the second-order basal reflection from the kaolin mineral in the fireclay at about 3·57–3·60 Å. Other anatase lines are weaker and may be overlooked or may be masked by reflections from other minerals present. X-ray photographs of artificially prepared kaolinite-anatase mixtures show that as little as 1 % of the latter mineral may be detected. Its presence is more definitely shown by heating the clay to 600° C. for 15–30 minutes when the kaolinite structure breaks down and the anatase lines are then more easily seen. In all cases where we have used this method we have found the full powder diagram of anatase. Anatase does not change to rutile unless heated to 800° C. or higher temperatures, depending on its mode of preparation (Pamfilov and Ivancheva, 1940; Thienchi, 1946). Some chlorites also give a line at about 3·5 Å., but they are usually revealed by a 14 Å. line and by a line at about 4·6 Å. of comparable intensity to the 3·5 Å. line. There should be no difficulty in distinguishing anatase from a possible chlorite. In the majority of fireclays which we have examined, anatase is still present when fine fractions approaching 1 μ in size are separated by sedimentation methods; in fact the anatase appears to be of comparable fineness to the kaolin mineral in the fireclay.

It would be out of place here to give a wide survey of references to the mineralogical form of titania in kaolin clays, but the following may be briefly mentioned; Ennos and Scott (1924) in their memoir (p. 4) record nineteen accessory minerals in clays including rutile but not anatase, and in a discussion of titania in clays state (p. 9), 'It generally occurs as microscopic or sub-microscopic crystals of rutile (TiO_2) or ilmenite ($FeTiO_3$).' Coon and Lewis (1926) discussing accessory minerals in pottery china-clays mention 'minute acicular crystals whose identification is ambiguous, probably rutile', but anatase is not mentioned. Gregory (1910) examined fireclays from Ayrshire and found 'abundant excessively small needles and granules of rutile', but he also did not record anatase. In a memoir on 'The Ayrshire bauxitic clay', Wilson (1922) states (p. 12) that 'small grains of rutile can readily be recognized' and that 'clusters of minute crystals . . . can be seen' which may be 'rutile, anatase and sphene'. De Lapparent (1934) has also examined the Ayrshire bauxitic clays; discussing the decomposition of ilmenite, which has come from basaltic fragments in the clay, he writes (p. 3), 'In the last stage of decomposition the titaniferous iron oxide has yielded anatase, which may be said to be the characteristic form which titanium oxide possesses in the bauxitic clays.' This is the only clear statement we have found in the literature that anatase rather than rutile is the normal form in which titania exists in fireclay deposits.

The clays we have examined fall into four groups.

I. *Fireclays from Ayrshire and Central Scotland.*—An Ayrshire bauxitic clay (exact locality unknown) has been examined together with the following six clays from Central Scotland: the blue clay at Glenboig, the clay immediately beneath it, and the black clay at Castlecary, all of which are part of the Upper Clay Seam of the Millstone Grit Series; samples of the Lower Clay Seam from Glenboig and Levenseat; and lastly the so-called 'cement clay' immediately underlying the cement stone horizon. In all these clays, X-ray photographs have shown the presence of anatase to the extent of 1–2 %. Chemical analyses have shown between 1 and 2 % of TiO_2, so that these amounts are probably wholly or largely anatase. These results provide direct confirmation of de Lapparent's results.

II. *Fireclays from the Carboniferous Coal Measures, mainly in Yorkshire.*—Fireclays from Halifax, Elland, Gildersome, Denholme, Tong, Ambler Thorn, Queensbury, and Ingleton in Yorkshire, and from Knowlbury in Shropshire have been examined and without exception all appear to contain anatase to the extent of about 1 %, although the quantity varies somewhat from one specimen to another. The conclusion may be drawn that in clays of this type anatase is commonly present; furthermore, sedimentation tests have shown that it is of comparable fineness to the kaolin mineral.

The following observations of Butterfield (1934, 1936) on the occurrence of anatase in sandstones of the Millstone Grit Series in Yorkshire may be noted: he writes (1936, p. 150), 'As a source of titanium minerals in the Grit ilmenite is a mineral to suspect . . . ilmenite has come into the Grits in large quantities. In many cases it is still found in fair abundance as fresh rounded grains, but more often it shows traces of alteration. . . . All stages in this alteration process can be followed from the partial alteration to complete replacement by leucoxene, and then further to the formation of tablets of anatase.' It seems not unlikely that a similar process may be responsible for the presence of anatase in the overlying Coal Measure fireclays.

III. Kaolinites from various sources throughout the world have been examined and in no case have we detected either anatase or rutile.

IV. Among miscellaneous clays, dickite may be included; neither anatase nor rutile has been detected in association with this mineral.

Finally, we wish to tender our thanks to all who have supplied us with specimens of clays and especially to Dr. F. A. Bannister for many kaolinites, to Professor A. L. Roberts for many Yorkshire fireclays, to Dr. J. E. Hemingway for kaolinites, dickites, and other clays, to Mr. J. McWilliam for the Central Scottish clays, and to Mr. A. T. Green, Director of the British Refractories Research Association, and Mr. A. E. Dodd of that Association for specimens of clays and for a memorandum on the occurrence of TiO_2 in clays. We also tender our thanks to the Department of Scientific and Industrial Research for a grant to assist a programme of research on clay mineralogy.

References.

Butterfield, J. A. (1934). The heavy minerals of the sandstones of the Snail Green boring. Trans. Leeds Geol. Assoc., vol. 5 (pt. 2 for 1932–33), pp. 97–111.

—— (1936). An occurrence of anatase (var. octahedrite) in the Millstone Grit of Yorkshire. Ibid., vol. 5 (pt. 3 for 1934–35), pp. 142–152. [M.A. **6**–533.]

Coon, J. M., and Lewis, E. J. (1926). On some pottery china clays and the granite from which they are derived. Trans. Ceram. Soc., vol. 25, pp. 490–499.

Ennos, F. R., and Scott, A. (1924). Refractory materials: Fireclays. Analyses and physical tests. Spec. Rep. Min. Res. Geol. Surv. Great Britain, vol. 28.

Gregory, J. W. (1910). The Glenboig fireclay. Proc. Roy. Soc. Edinburgh, vol. 30, pp. 348–360.

Lapparent, J. de (1934). La boehmite et le diaspore dans les fireclays de l'Ayrshire (Écosse). Compt. Rend. Acad. Sci. Paris, vol. 199, pp. 1629–1631 [M.A. **6**–135]; also Summ. Progr. Geol. Surv. Great Britain, for 1934, pt. 2, pp. 1–7.

Pamfilov, A. V., and Ivancheva, E. G. (1940). On the chemistry of titanium. Part XVI. The transition from the anatase to the rutile structure. (Russ.) Zhurn. Obshch. Khim., vol. 10, pp. 736–744. [M.A. **8**–182.]

Thienchi, N. (1946). Transformation de l'anatase en rutile. Compt. Rend. Acad. Sci. Paris, vol. 222, pp. 1178–1179. [M.A. **10**–184.]

Wilson, G. V. (1922). The Ayrshire bauxitic clay. Mem. Geol. Survey, Scotland, 1922, 28 pp.; and Trans. Geol. Soc. Edinburgh, 1923, vol. 11, pp. 255–256. [M.A. **2**–556.]