

*The natural history of Kaolinite.*

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IN the south-west coal-field of east Glamorganshire—especially in the Lower Coal Measures—Mr. A. Tait, of Caerphilly, observed last year a white, soft, and pulverulent substance, saponaceous to the touch. A specimen sent to me, examined first and identified by Mr. T. Crook, was found to consist of a congeries of well-defined crystals of kaolinite. The crystals are chiefly basal flakes, hexagonal in outline, and 0.02 to 0.037 mm. in length. Most of them show elongation in one direction, and unequal extension of the thin lamellae composing them.

Mr. Crook has kindly provided me with the following details in proof of the identity of the mineral:—

‘The specimen consists of a white, crystalline powder, and is seen, on examination with the microscope, to be made up almost entirely of small hexagonal plates and *rouleaux* of the same, which have the characteristic form and appearance of kaolinite. The maximum refractive index is less than 1.57, and the minimum greater than 1.56. Plates lying flat against the slide show a refractive index of very nearly 1.56 and exhibit little or no birefringence. In composition, the material is hydrated silicate of aluminium. A determination of water by loss on ignition, in a portion practically free from calcareous and carbonaceous matter, gave 18.78 per cent.’

The strata that carry the kaolinite are situated beneath some 200 feet of Pennant Grit. They comprise coal-seams, grits, fire-clays of varying degrees of purity, highly carbonaceous clayey shales, and hard shales locally called ‘clifts’.

The changes that have taken place in the grits since their deposition have precluded the positive identification of kaolinite in microscopic sections prepared for the author. A grit taken from a depth of about 500 feet from the surface proved to be similar to the Pennant, except in presenting here and there minute pellets of altered dolerite, and in being rendered much darker in tint by diffused carbonaceous matter. Both rocks consist of angular quartz-grains set in a paste of decomposed

felspar, quartz, and abundant muscovite-mica. The mica is almost wholly such as results from the decomposition of felspars—a felt-work of ill-defined lenticular scales. These enwrap the quartz-grains, and are clearly of secondary origin. The remainder of the mica occurs in scattered fragments, whose regular outline and straight cleavage-traces imply derivation from a phyllite. In the interstices of the mica are little patches of granules that, owing to the close resemblance of cryptocrystalline quartz and kaolin, it is hazardous to pronounce upon definitely, although some exactly resemble the microscopic kaolin of various Cornish rocks.

The kaolinite may be traced, as specimens indicate, through every accessible bed of rock in the Measures: it may be seen lying along the cleavage-planes of the coal at a depth of 560 yards from the surface. The most abundant deposits, varying in thickness from that of a slight film to a quarter of an inch, form the central band in vertical fissures in the grits, which are lined with quartz and dolomite or calcite, and may be studded with pyrite and millerite crystals. Obviously the kaolinite was the last mineral to occupy the fissures. In places, more particularly along fault-planes, it is admixed with muddy and other foreign material. Its usual freedom from impurities and its loose state of aggregation probably point to quiet deposition from suspension in water that percolated through the Coal Measures.

The occurrence of kaolinite, either as a constituent or as a deposit, in Carboniferous and other sedimentary rocks has been repeatedly noted.<sup>1</sup> Its mode of origin in the Coal Measures is a problem to which it appears desirable to devote a few words.

R. Lang, in his account of the Middle Keuper Sandstones of Swabia,<sup>2</sup> effectually proves that their contained kaolinite is not a product of the weathering of felspar, the decomposition of the latter mineral having there been brought about by intra-telluric waters charged with carbonic acid. In the absence of proof that kaolinite once formed is capable of being dissolved by any acidulated or other waters known to exist in sedimentary rocks, it seems difficult to accept his view that the kaolinite of certain decalcified sandstones was deposited from solution in cavities vacated by calcite. One is tempted to surmise that the original felspar of the sandstones described was akin to bytownite or anorthite in composition, and suffered metamorphosis into calcite and kaolinite.

<sup>1</sup> See A. Lacroix, 'Minéralogie de la France,' 1895, vol. i, pp. 467-470.

<sup>2</sup> R. Lang, *Centralblatt Min. Geol.*, 1909, pp. 596-599.

As regards the Glamorganshire kaolinite, we may be certain that it is not a product of the weathering of the felspar-constituent of its parent rocks by surface-waters charged with sulphuric acid resulting from the oxidation of disseminated iron sulphide. The thickness of the cap of Pennant Grit, and its freedom from ferric iron, as intimated by its tint, also the abundant carbonaceous matter dispersed throughout the Measures, and the brightness of the pyrite wherever it occurs preclude the supposition that the oxygenation characteristic of weathering was operative during the chemical changes that produced the kaolinite.

We are restricted consequently to the conclusion that the kaolinization of the felspar of the rocks of the coal-field was the work of carbon dioxide in solution, that gas being a constant emanation from the coal-seams and carbonaceous shales, particularly those subjected to an elevated temperature at great depths. The existence of dolomite and calcite in the fissured grits is, in fact, sufficient evidence that the water in the Measures has been acidulated by carbon dioxide. That the kaolinite was of very slow growth is probably to be inferred from the geometric perfection of its crystals.

What we note in the Glamorganshire coal-field is essentially that which, according to C. Gagel,<sup>1</sup> H. Stremme,<sup>2</sup> E. Weiss,<sup>3</sup> F. Wüst,<sup>4</sup> and others, has been brought about in the upper regions of granitic masses by the carbonic acid of underground springs or of moor-water that has percolated through bogs, and has taken up in addition the humus-compounds crenic and apocrenic acids. Stremme remarks that weathering and kaolinization are produced only by weak acids at a somewhat low temperature, notably by solution of carbon dioxide, weathering being carried on with the co-operation of oxygen, and kaolinization in its absence, and presumably sometimes under the influence of reducing agents. That heated subterranean waters may contain carbonic acid he does not dispute, but he is of opinion that this would speedily be removed from action by combining with the salts dissolved thereby.<sup>5</sup>

Except as regards the source of carbonic acid, precisely similar chemical considerations seem to be necessitated in discussing the origin, on the

<sup>1</sup> C. Gagel, *Centralblatt Min. Geol.*, 1909, pp. 437 and 467-475.

<sup>2</sup> H. Stremme, *Zeits. prakt. Geol.*, 1908, vol. xvi, pp. 125-128.

<sup>3</sup> E. Weiss, *ibid.*, 1910, vol. xviii, pp. 353-367.

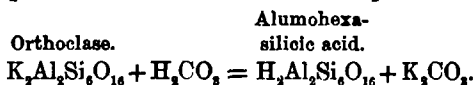
<sup>4</sup> F. Wüst, *ibid.*, 1907, vol. xv, p. 19.

<sup>5</sup> H. Röslér, *Zeits. prakt. Geol.*, 1908, vol. xvi, p. 251, questioning the correctness of Stremme's description of a bed of altered rock as kaoliniferous, observes that it contains what appears to be a scaly sericitic mineral. That this has resulted from chemical change in kaolinite seems quite possible.

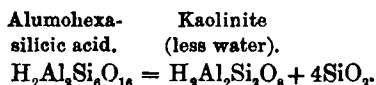
one hand, of the kaolinite and secondary muscovite and quartz of the kaolin-rock and greisens of Cornwall, and, on the other, of the kaolinite, mica, and quartz cement of the grits of the Welsh coal-field.

J. Morozewicz<sup>1</sup> has suggested that kaolinite, which has the composition  $H_2Al_2Si_2O_8 \cdot H_2O$ , may, without its water of crystallization, be regarded as the first of a series of acids of which cimolite and pyrophyllite are respectively the second and third members. These have the general formula  $H_2Al_2Si_nO_{2n+4}$ , and yield the ions  $H_2$  and  $Al_2Si_nO_{2n+4}$ . When  $n$  exceeds 4 the silicic acid is readily broken up. Orthoclase is the potassium salt of alumohexasilicic acid,  $H_2Al_2Si_6O_{16}$ , the fifth member of Morozewicz's series.

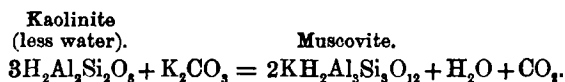
These premises furnish us with a clue to the transformations effected by carbonic acid in contact with orthoclase. We have first the conversion of the felspar into alumohexasilicic acid and potassium carbonate:—



The acid, breaking up, yields kaolinite and silica:—



The potassium carbonate in the presence of the kaolinite, or aluminosilicic acid, produces muscovite, water, and carbon dioxide:—



Carbon dioxide is thus seen to act merely as a carrier of the alkali metal: what is not removed by flow of aqueous solution or entangled in nascent silica is free to recommence the decomposition of orthoclase. Granted, therefore, a sufficiency of time, it appears unnecessary to postulate the presence of more than a comparatively small proportion of carbon dioxide for the conversion of vast quantities of felspar into an admixture of kaolin and muscovite.

For simplicity's sake no attempt has above been made to suggest the nature of the interaction of compounds of lithium and fluorine with kaolinite to form the micas of the china-clay districts of Devon and Cornwall.<sup>2</sup> Though boron must have been very generally present in the

<sup>1</sup> J. Morozewicz, *Kosmos*, Lemberg, 1907, vol. xxxii, p. 496; for abstract, see *Zeits. Kryst. Min.*, 1910, vol. xlviii, p. 523.

<sup>2</sup> On the constitution of the micas, see F. W. Clarke, *Bull. United States Geol. Survey*, 1895, No. 125, p. 45.

magmas of the acidic igneous rocks of those counties, the possibility of fluorization quite apart from boration is distinctly there indicated by the existence of schorl-free greisen with topaz and schorl-free china-stone with fluor-spar and apatite.<sup>1</sup>

The earthy or poorly crystalline condition of the kaolinite of china-clay is presumably assignable to rapidity of production due to warmth. Lack of space for molecular movement during pseudomorphism not involving much loss of bulk and the presence of foreign matter (as exemplified in the distortion of ice-crystals formed on London pavements) may, however, have both adversely influenced the crystallization of kaolinite in china-clay.

If the genesis of kaolinite from felspar through the agency of carbonic acid may by now be regarded as proved by the results of a multitude of independent observations, including those of Bischof,<sup>2</sup> the upholders of Daubrée's hypothesis—that it is due to decomposition of felspar by boric and fluoric acids—are somewhat arbitrarily demanding the acceptance of two widely different explanations of one and the same chemical operation, i. e. the conversion of an anhydrous into a less-complex hydrous silicate.

A prolific source of error with respect to the nature and the period of the origin of kaolinite has been the frequent close association of kaolin with the products of tourmalinization—a process of repeated occurrence in the history of events in the geology of the west of England. There the existence of kaolin in commercially important quantities as a product of the alteration of granite is a purely local feature, referable to one period of pneumatolysis. Boration in addition to fluorization, however, can be shown to have taken place at various periods. Tourmaline, its commonest product, occurs in scattered crystals in granite both as an original constituent and as a substitute for primary biotite; also (in the radiating and acicular form) it replaces the micas and feldspars of unkaolinized granites<sup>3</sup> and elvans, and the china-clay of kaolin-rock. This species of pneumatolysis, moreover, has not been confined to limited areas or to acidic igneous rocks only. The whole basis of the sedimentary strata of Cornwall and west Devon must in times gone by have been besieged by borated and fluorated liquids and vapours at no low tempera-

<sup>1</sup> For other examples of fluorization see F. H. Butler, *Mineralogical Magazine*, 1908, vol. xv, pp. 139-141.

<sup>2</sup> G. Bischof, 'Chemische Untersuchung der Mineralwasser zu Geilnau, &c.,' Bonn, 1826, pp. 302-309. See also J. S. Flett, *Mem. Geol. Survey*, 'Geol. of Bodmin and St. Austell,' 1909, p. 118, par. 2.

<sup>3</sup> J. J. H. Teall, 'British Petrography,' 1888, p. 314.

ture, and ready under pressure to sally forth along planes or channels of weak resistance. Thus, we find that tourmalinization did not take place merely along the contact-zones of sedimentary and igneous masses, and where kaolinization had facilitated the formation of fissures.<sup>1</sup> It played also an important part in the production of much lode-material in districts widely separated from the china-clay areas. It was, in addition, largely concerned in a far-reaching sporadic metamorphism of rocks, developing schorl in non-calcareous killas, axinite in calcareous killas, the Culm Measures, and doleritic intrusives, and datolite at the junction of serpentine with a hornblende-schist,<sup>2</sup> or deformed and metamorphosed enstatite-gabbro.

What has frequently proved a hindrance to the correct interpretation of episodes in the geological history of the west of England china-clay areas is the variety of appearances produced in constituents of rocks according to their distance from the main path of flow of a succession of pneumatolysing agents. Thus we find at Shilton, St. Austell, ordinary kaolinized granite passing almost abruptly into a rock with a groundmass composed of secondary white mica, schorl, and abundant highly vesicular quartz. The quartz is crowded with irregular liquid vesicles and negative crystals, each with a good-sized gas-bubble, and many a one with also a small cubic crystal. The larger china-clay pseudomorphs after orthoclase are replaced by a pearly white mica or by compact gilbertite. The gilbertite and white mica were clearly formed by a pneumatolysis, similar to that which occasioned the paragenesis of those minerals in the St. Stephens district. The gilbertite may be seen to have grown from within outwards, and to have been formed before the crystallization of the schorl, for the schorl skirts without penetrating it. The smaller china-clay pseudomorphs that, being near the ordinary kaolin-rock, have not been dissolved away or converted into constituents of the groundmass, show little change into gilbertite, possibly from the rapid leaching-out of basic constituents required for the formation of that mineral.<sup>3</sup>

<sup>1</sup> See Mem. Geol. Survey, 'Geology of Bodmin and St. Austell,' 1909, p. 108. The map of the St. Austell granite there given shows strikingly irregular extension of the kaolinized areas alongside the included tin-lodes—a feature favouring the view that kaolinization took place quite independently of and previous to the formation of the lode-fissures.

<sup>2</sup> W. F. P. McLintock, *Mineralogical Magazine*, 1910, vol. xv, pp. 407-408.

<sup>3</sup> The presence in china-clay of small quantities of bases not contained in kaolinite has been repeatedly demonstrated. Four samples of Cornish china-clay of the best quality analysed by W. Jackson and A. G. Richardson (*Trans. English Ceramic Soc. Tunstall, Staff., 1905, vol. iii (1903-4), p. 56*) gave an

Where pneumatolysis was most active in the Shilton rock and caused the rapid removal of kaolin, the place of mica is occupied mainly by quartz, gilbertite, and cassiterite; and the china-clay pseudomorphs after felspar are represented by cavities into which project needles of schorl, misshapen crystals of quartz, a little gilbertite, and abundant cassiterite. The deposition of the gilbertite in these cavities must have been coincident with that of cassiterite, for shapely crystals of it may be seen both alongside of and perched on the latter, as in some specimens of Zinnwald ore.

In St. Austell parish and elsewhere in the Hensbarrow district occur many other instances of the post-kaolinization boration of china-clay rock, proceeding along both sharply defined flat-walled fissures and irregular channels. The evidence of the kaolinized granites of the west of England is, in short, opposed to the opinion, adopted by some writers,<sup>1</sup> that their kaolinization was subsequent to the extensive tourmalinization to which wide tracts and broad courses and numerous veins of schorl and schorl-rock bear witness—an opinion obviously fostered by the persuasion that the china-clay of commerce must have been produced by the weathering of felspar.

G. S. O. Lasius<sup>2</sup> in 1789 first drew attention to the occurrence of schorl in the Harz Mountains at the contact of granite with other rocks; but it does not appear that he came upon any associated kaolin. He remarked that the schorl is a constituent also of mineral-veins in the vicinity of the granite, and that for this and other assigned reasons he was disposed to class it with lode-minerals. The significance of these observations appears to have escaped recognition by those who after his time attributed the kaolinization of granite to a pneumatolysis such as would produce tourmaline. Otherwise, taking cognizance of the fact that wherever metallic ores occur together with schorl in the china-clay districts of the west of England there is evidence of the work of pro-

average composition of alkalis 2.785, CaO 0.13, MgO 0.12, Fe<sub>2</sub>O<sub>3</sub> 0.625 with SiO<sub>2</sub> 46.127, Al<sub>2</sub>O<sub>3</sub> 38.09, and water 12.157, in a total of 100.034. The proportions of the different mineral constituents were: clay-substance 97.372, quartz 0.89, felspar 1.685, in a total of 99.95. Still larger amounts of bases other than alumina were obtained in some of W. I. Macadam's analyses: see *Mineralogical Magazine*, 1886, vol. vii, p. 76.

<sup>1</sup> Cf. G. Hickling, *Trans. Manchester Geol. and Mining Soc.*, 1908, vol. xxx, p. 355; and *Mem. Geol. Survey, 'Geology of Land's End,'* 1907, p. 58, par. 3.

<sup>2</sup> G. S. O. Lasius, 'Beobachtungen über das Harzgebirge,' 1789, Theil i, pp. 77-80.

cesses destructive of kaolin, they might have been led to question how the kaolinizing medium could have been that which generated the schorl.

To contend that because boron compounds, the results of a special kind of pneumatolytic action, occur in various rocks containing kaolinite, kaolinization is due to that action is an assumption that scarcely lends itself to the logic of facts.

Since the above was written the author has been favoured by Dr. J. S. Flett with a specimen of fine-grained Kinder Scout Grit (a division of the Millstone Grit) from Bamford Edge, north Derbyshire, thirteen miles south-west of Sheffield. From its altered felspar good kaolinite crystals can be teased out with a needle. In microscopic preparations the rock shows, interspersed among particles of quartz and a little unaltered albite, abundant fragments of orthoclase in various stages of decomposition into kaolinite. Crystals of kaolinite fleck the surface of the sections of felspar, or, less commonly, occur as an interstitial substance filling what seem to have been original cavities in the rock. Besides the kaolinite some of the felspars contain many small specks of mica, a few small clusters of which are also here and there perceptible in the cavities containing kaolinite. Between crossed nicols the higher polarization tints of the mica serve to distinguish it from the colourless kaolinite. This rock may be regarded as presenting the initial stages of the formation, by the agency of carbonic acid, of kaoliniferous grits such as those of the Glamorganshire coal-field.

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