On the Nature and Origin of Clays: the Composition of Kaolinite.

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THE clays appear under many widely different aspects, and from one point of view must be studied as rocks. There are rock-masses alike of clay and of serpentine, both the result of important metamorphic processes. The basis, however, of most—probably of all—clays appears to be a substance of definite composition and well-marked characters, as much entitled to specific mineral rank as allophane or serpentine, or perhaps opal. In this paper I propose to consider clay as a rock and as a mineral.

1. *Clay as a rock.*—The kaolinisation of felspar, the incipient stage of which is indicated simply by a peculiar opacity, as in the case of the granitic rocks of Cornwall and West Devon, is sometimes very complete, and occurring over large areas results in the shape of kaolin or China-clay, or potter's and brick-clay. Such productions may be conveniently studied according as they occur *in situ* or are derived and transported.

a. Clay-masses in situ.—The chief of these is the rock known as China-clay-rock or *Carclazyte*,[1] composed of white or greyish-brown quartz, white lepidolite or gilbertite, and white orthoclase, the last more or less completely kaolinised. As accessories, schorl and brown mica (lepidomelane) are common, and cassiterite and topaz not rare. The form of the felspar crystals, often clearly distinguishable, is usually the Carlsbad macle. The China-clay-rock seldom extends more than a few fathoms on either side of the schorlaceous veins in which kaolinisation seems always to have originated, but may accompany them to a depth of 100 fathoms or more from the surface. Several of the largest China-clay works in Cornwall—as at Carclaze and Beam—were at first opened on such veins for the tin they contained.

"China Stone," or Petuntzyte,[2] is a rock similar to but less completely altered than Carclazyte, its usually abundant felspar retaining some alkali.

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[1] J. H. Collins, F.G.S., 1878. The Hensbarrow Granite District.

[2] *Hensbarrow Granite*, p. 31. This substance is ground up with clay and other ingredients in the manufacture of porcelain.

There is often a little fluor present, and the presence of white lepidolite ("shell"), and brown or black schorl may detract from or neutralise the economic value of the rock. In the parishes of St. Stephen's and St. Dennis, near St. Austell, and at Tregoning Hill, in Mount's Bay, China-stone, like the China-clay-rock, occurs in irregular bands or patches. Though as yet never worked more than a few fathoms from the surface, it is believed to continue in depth. In several localities it overlies China-clay, which it very rarely caps.[1]

The kaolinisation noticeable in the "decomposed elvans"—mostly altered felsites, quartz-porphyries, or felspar-porphyries—affords excellent material for crucibles and fire-bricks, but is practically useless as a source of China-clay.

b. *Derived Clay.*—Of these the following may be taken as typical examples :—

(1.) *Flucans of Mineral Veins.*—These commonly observable unctuous clay-partings or vein-fillings are among the most common phenomena. They are the product of former continued earth movements, or a sediment from fluids.

(2.) *Bovey Tracey Clay Deposits.*—These beds, interstratified with lignite, by their situation at the base of the extensively kaolinised granitic rocks of Dartmoor, suggest a derivation from those rocks by a process of natural clay-washing into a depression then occupied by a lake. The pipe-clay and potter's clay of Dorsetshire have had a somewhat similar origin.

(3). *London Clay.*—The abundance of the foreign matter in this clay is plainly due to the distance of its place of origin from that of its deposition. Mr. Sorby's remark that "the chief portion of the fine-grained clays cannot be distinguished from the products of the decomposition of felspars and other minerals which can be changed in a similar manner,"[2] I have found true in every case where I have examined clays by combined chemical and mechanical methods.

2. *Clay as a Mineral.*—The objections to regarding clay as a mineral may be reduced to two :—1st. That a crystallised or crystalline condition is a necessary character for a mineral species ; and 2nd, that the clays are not of definite chemical composition. But, by common assent, such amorphous

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[1] Professor Sedgwick (*Camb. Phil. Trans.* I. pp. 104-5) says—speaking of decomposed granite-rock in general—"on a near examination it is frequently found soft enough to be cut with a spade—and it is *in that state* packed up and exported to the potteries." As a matter of fact China-*stone*, which is exported to the potteries in its raw state, is never soft enough to be cut with a spade ; while China-*clay*, which may be so cut, is never so exported.

[2] Sorby: *Anniversary Address to Roy. Micros. Soc.* 1877.

substances as allophane and gibbsite are admitted to specific rank, while the supposed variations in the chemical composition of clays result from the error of chemists in analysing manifestly impure mixtures instead of China clay,[1] which, freed from foreign bodies, has a composition agreeing very closely with that of Dana's "Kaolinite." The more perfectly an impure clay-mass is cleansed, the more nearly does the resulting material agree in composition and physical characters with that of the best commercial China-clay.

The inclusion of other minerals in natural felspar crystals, and possibly too in some instances the introduction of new substances by the kaolinising solutions, causes the final product of their change to be a mixture of two or more distinct minerals. Completely decomposed felspar, as shown by our former President, Dr. H. C. Sorby, "breaks up into granules of kaolin from $\frac{1}{6000}$th to $\frac{1}{50000}$th of an inch diameter, which have a refractive power so nearly that of Canada balsam that they are best seen when mounted or suspended in water. They are not, strictly speaking, amorphous, nor yet minute crystals, but somewhat flattened and elongated particles very similar to those obtained on reducing undecomposed felspar to a fine powder; as though the original crystalline structure had had a very powerful influence in determining their shape. The depolarising power is very high, and can be easily recognised in particles as small as $\frac{1}{12000}$th of an inch in diameter."[2] So fine are some of the particles, that when suspended in pure water they take five days to subside one foot in depth.[3]

Amongst the granules of decomposed felspar Mr. Sorby found some small needle-shaped crystals, the nature of which he did not determine, but which, if the kaolin he was examining came from Cornwall or Devon, were probably achroite. Besides these, small hexagonal or irregular scales or fibrous looking aggregates of micaceous minerals, as well as minute siliceous grains, are frequent.

At the present time more than a quarter of a million tons of China-clay are annually prepared from decomposed granite in Cornwall and Devon, besides smaller quantities in Germany, France, Spain, the United States, and notably China and Japan. The analyses given in Tables I. and II. will show how little diversity of composition there is throughout the im-

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[1] This is true of nearly all the analyses given by Prof. Macadam in No. 33 of the *Min. Mag.* p. 76. and notably of Nos. 1 to 7, 10 to 15, and 20 to 27. Boase's analysis of kaolin, quoted by Mr. Butler at p. 79 of the same No., was evidently made on faulty material, as is shown by the enormous quantity of alkali.

[2] Address to the Royal Microscopical Society, 1877.

[3] *Ibid.* 127.

mense series of English China-clays; and the foreign examples examined are quite comparable with these.

TABLE I.

Analyses of Commercially Dried China-Clay.

	M. xxx. *	No. 2. Do. L. M.	No. 1. Do. L. M. *	R.	B. C. *	L. M.	L. H. B.	Treverbyn A.	Treverbyn B.	Tremayne. No. 1. Yellow.	Do. No. 2. White.
SiO_2 ……	46·60	46·90	41·60	47·84	45·60	45·90	45·83	45·75	45·38	45·40	43·50
Al_2O_3 ……	39·60	38·35	36·60	38·76	39·12	40·40	40·36	40·68	40·11	40·50	40·00
Fe_2O_3 ……	·10	·09	·07	·11	·08	·04	·07	·03	·02	·12	·12
Alkalies ……	·21	1·38	1·56	—	—	—	—	traces	1·17	—	—
MgO ……	—	—	—	—	—	—	—	} 0·48	0·36	} —	—
CaO ……	—	—	—	—	—	—	—			—	—
H_2O ……	13·03	12·55	19·37	12·67	13·51	13·21	12·42	13·01	12·62	13·20	13·40
	99·54	99·27	99·20	99·38	98·31	99·55	98·68	99·95	99·66	99·22	97·02

	M. B.	St. Day.	Carludden, June 1876, very dry.	Menyridden, June 1876, very dry.	W. B. 1876. *	Rosemellyn.	Rosemellyn.	Treviscoe. common. *	Treviscoe. very common.	Bohemia.	Bohemia.
SiO_2 ..	45·4	45·2	49·1	46·2	46·5	45·89	46·00	49·8	48·14	43·90	48·14
Al_2O_3 ..	40·2	37·8	40·2	41·1	40·2	41·71	39·86	36·9	37·71 }	38·33 and loss	41·48
Fe_2O_3 ..	tr.	1·5	·4	·2	·3	·12	·13	·5	·70 }		
Alkalies ..	·6	1·2	—	·5	·6	—	—	·2	—	4·85	·10
MgO ..	tr.	—	·2	·2	·3	tr.	tr.	·4	—	·10	·10
CaO ..	tr.	—	—	—	—	—	—	—	—	—	—
H_2O ..	13·5	12·5	10·3	12·5	13·0	12·80	12·70	12·0	12·20	12·82	10·18
	99·7	98·2	100·2	100·7	100·9	100·52	98·69	99·8	98·75	100·00	100·00

The above were commercially dried clays, mostly of good quality and fairly well washed. The percentage of water varies from 10·18 up to 19·37 per cent., or excluding the third which was distinctly moist, up to 13·51, the average being 12·62. The 26 analyses given by Dana range from 12·47 to 15·90, the average being 14·13. All had been dried by artificial heat in the process of manufacture, and subsequently exposed to the atmosphere. The water was determined in the ordinary way by drying at 100° C, but as I had some reason to suppose that some moisture was still retained, those marked (*) were specially dried and again analysed, with results as in Table II.

TABLE II.

ANALYSES OF CHINA-CLAY. (Dried *in vacuo* over Sulphuric Acid.)

	M. B. xxx.	*No. 1 L. M.*	*B. C.*	*W. B.* 1876.	*T. Comm.*
Silica ...	48·10	46·10	47·40	47·82	50·60
Alumina ...	41·00	40·60	40·52	41·43	37·60
Ferric Oxide	·10	·09	·09	·30	·49
Alkalies ...	·21	1·62	·10	·39	·20
Magnesia ...	trace	trace	·25	·29	·41
Lime ...	trace	trace	·22	·11	·10
Organic Matter soluble in Alcohol.	·02	·10	·04	·10	·10
Water ...	10·13	10·77	10·61	10·50	10·40
	99·56	99·28	99·23	100·94	99·90

Here the range is very small and the average percentage of water is but 10·5. This may be still too high, although I do not think it is; it cannot possibly be too low.

In the large number of samples of China-clay from different countries which I have analysed and examined during the past 15 years, I have noticed two characteristics:—

1st. An entire absence of scaly or flaky particles when the clay has been adequately washed. These foreign bodies are pretty easily separated, especially in bulk. True kaolin, instead of being "made up largely of pearly scales" (Dana), is in general, and always when properly prepared, absolutely free from them. The hexagonal scales "which may be detected in all [improperly prepared] kaolin," on which Johnson and Blake, followed by Dana, founded their orthorhombic mineral kaolinite, do not appear to have been separated and analysed. They may, indeed, be identical with the Anglesea kaolinite, or they may be lepidolite, gilbertite, nacrite, or sericite, for anything which appears in their paper.[1]

2nd. A great uniformity of composition. This is shown in the foregoing analyses.

Furthermore, it seems well-nigh impossible to make the composition agree with the typical formula adopted by Dana, and after him by most other writers on mineralogy. China-clay properly purified by careful washing, when dried *in vacuo* has invariably a composition very closely agreeing with that given under *a*, Dana's type composition being as under *b*.

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[1] See S. W. Johnson and J. M. Blake. *Am. Journ. Science*, 2nd series. Vol. 43, p. 351.

	a.	b.
Silica	48·0	46·3
Alumina	41·2	39·8
Water	10·8	13·9
	100·0	100·0

The discrepancy here observed may appear small for an amorphous substance; but I think it is of such a nature as both to prove the inaccuracy of Dana's deductions and to point to a more simple formula.

The composition given in *a* answers to the formula $Al_2H_6O_6SiO_2 + Al_2O_3$, $3\ SiO_2$; in other words, one half of the alumina is present as hydrated silicate, the other half as an anhydrous tersilicate. Dana's formula, on the contrary, is $2\ (\frac{1}{4}\ H_2O_3\frac{3}{4}Al_2O_3)\ 3\ Si\ O_2$, or Al_2O_3, $2\ SiO_2 + 2\ H_2O$—in other words, all the alumina is in the same state of combination.

Now experiment supports the first formula; for if kaolin be treated with hot sulphuric acid, about half of the alumina is at once dissolved out: the other half remains in combination with the silica, but may be very slowly got out by repeated treatment with the acid.

That Dana's adopted percentages are wrong is shown, I think, by his own table, which gives, out of 26 analyses, no fewer than 6 having the alumina *above* the type proportion as it stands, besides many others where it would be in excess if extraneous matter were eliminated, or if the totals of silica, alumina, and water were calculated up to a total of 100. This would be still more noticeable if the water were to be reduced by about 3 per cent., as it should be according to the indications afforded by Table II. on the preceding page. Making these various corrections the average alumina in Dana's table comes out very close to 41 per cent.

I may here remark that the composition of the Anglesea kaolinite, first determined by Mr. Charles Tookey,[1] if corrected about 4 per cent. for (assumed) retained moisture, as under *c*, agrees with *d*, which is almost identical with the type analysis *a* already given.

	c.	d.
Silica	46·53	48·56
Alumina	38·93	40·90
Water	14·94	10·94
	100·40	100·40

If this be accepted as the true composition of the mineral, then the kaolinite of Dana may be looked upon as the crystalline form of kaolin.

That some correction for moisture is necessary is evidenced by the

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[1] See *Percy's Metallurgy*, *Introduction*, *Refractory Materials*, *&c.*, 1875, p. 93.

pearly lustre of the mineral, generally a sign of hydration. But there is some reason to believe that a larger correction for moisture is necessary, for a sample which I was enabled to examine by the kindness of Dr. Percy, after preservation for many years by him, gave when dried over sulphuric acid *in vacuo* only 8·40 per cent. of water.

3. *The Process of Kaolinisation.*—China-clay rock and China-stone have usually been referred to as "decomposed" or "disintegrated," and many writers have briefly referred to kaolinisation, treating of the occurrence of tin-ores, or of atmospheric effects upon rocks. These writers may be grouped as follows:—

a. Those who speak of "talcose-granite" or "protogine"[1] as the source of kaolin. "Protogine" as defined by these writers, viz. a compound of *quartz, felspar*, and *talc*, is now known to have been founded on a mineralogical mistake. I have as yet never met with a granite containing so much as two *per cent.* of magnesia, which is usually present only in traces, or altogether absent. Certainly there is no such thing as *talc, talcose-granite*, or *protogine*, in the kaolin districts of the West of England, where probably gilbertite has been mistaken for talc.[2]

b. Another class of writers, as Page,[3] for instance, confound the decomposed rock with its later-formed derivatives. As I have elsewhere shown, kaolin is not found in beds and masses along stream-courses, and the richest and purest deposits do not occur in low grounds or farthest from the sources of disintegration. On the contrary, the only kaolin pure enough to be used commercially is obtained from the hills, and *in situ*.

c. Yet other writers attribute the metamorphosis of felspar to carbonic acid gas, acting from above or below.[4] This is probably efficacious as

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[1] Hawkins. *Trans. Roy. Geol. Soc. Cornwall*, IV. p. 372, &c.
Henwood. *Ibid.* V., pp. 17, 43, &c.
Lyell. *Students' Geology.* 1st edition, 1871, p. 541, &c.

[2] The composition of these two minerals is as follows:—

	Gilbertite, from Stenna Gwynn.	*Talc.*
Silica ...	45·10	62·58.
Alumina ..	36·00	—
Ferrous Oxide	1·10	1·98.
Lime ..	1·50	—
Magnesia ..	·91	35·40
Potash ..	11 40	—
Fluorine ..	·54	—
Water.. ..	3·70	0·04.
	100·24	100.00.

[3] *Economic Geology*, p. 184.

[4] Lyell: *Principles of Geology*, I. p. 413, 1867.

regards the kaolin of Auvergne, where there is a "continual disengagement of carbonic acid from numerous fissures;" but it seems to me that the entire absence of this gas and of carbonates in the clay districts of Cornwall and Devon affords a plain indication that, here at least, some other metamorphic agent has been at work, since all the phenomena indicate that the action has been from below.

d. Von Buch and Daubrée believe that kaolinisation is produced by fluids containing fluo-silicates or fluo-borates acting from below, generally if not always through fissures. There is no proof that such fluids are now present in the fissures, but the frequent occurrence in granites and porphyries of *schorl*, *topaz*, *gilbertite*, and other minerals containing fluorine, led these geologists, as well as Elie de Beaumont, to conclude that when oxide of tin was associated with them its presence was due to the same element. In support of this view Daubrée cites his production of crystals of oxide of tin by passing vapours of stannic chloride and steam through a heated porcelain tube.[1]

Von Buch early observed the constant occurrence of kaolin with minerals containing fluorine, and suggested that the kaolin of Halle owed its origin to hydrofluoric acid.[2] Daubrée, writing of the kaolin near St. Austell, remarks that it must have had a very similar origin.[3]

The decomposed granite of Cornwall and Devon is generally if not invariably accompanied by lepidolite containing fluorine. There is also almost always schorl, and very frequently gilbertite, and sometimes topaz or fluor-spar. This latter is scarce, I believe, only because of the absence of lime, as already intimated. Briefly, we may say fluorine is *always* present in some form or other, a fact strongly in favour of Von Buch's theory. Furthermore, it would appear that the action of fluorine and boron on oxide of iron in the presence of silica has resulted in the almost universal presence of schorl, and where lime was present we have now fluor-spar.[4]

4. *Artificial Kaolin.*—Having fully considered kaolinisation from the point of view of Von Buch and Daubrée, I naturally tried experiments

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[1] *Annales des Mines*, XX. 1841. He used perchloride of tin, as being more readily obtained than the corresponding fluoride; but he argues, and few chemists will dispute it, that similar results would follow from the use of the fluoride. The use of the chloride instead of the fluoride may explain why the artificial oxide differed in form from the natural.

[2] *Min. Tasch.* 1824.

[3] *Ann. des Mines*, 1841.

[4] See, for fuller details, my paper on "Cornish Tinstones and Tin Capels," *Min. Mag.* IV. pp. 123, 124, 1882.

on felspar and granite with hydrofluoric acid. I at first employed a leaden tube at a high temperature, through which the vapour acid was passed. As was to be expected, the felspar was rapidly converted into hydrated silicate of alumina, mixed with soluble fluoride of potassium, while pure silica was deposited on the sides of the tube.[1] In later experiments, I have found it preferable to use a dilute solution of hydrofluoric acid at ordinary temperatures. Contrary to what is generally stated, orthoclase seems to be much more readily and completely affected by fluorine than either albite or oligoclase. Labradorite is decomposed only in spots, obsidian also, but very slightly. It is probable that a great many minerals are capable of being thus "kaolinised," and not merely the felspars, The following analyses show what was effected by 96 hours' treatment of orthoclase with hydrofluoric acid at a temperature of 60° F :—

	a.	*b.*	*c.*
Silica	63·70	49·20	44·10
Alumina ...	19·76	35·12	40·25
Potash ...	13·61	·12	·25
Soda	2·26	trace	trace
Ferric Oxide ...	·71	trace	trace
Water	trace	14·20	15·01
	100·04	98·64	99·61

a. is the original felspar analysed by Mr. A. H. Church.

b. is my analysis of the inner layer of the altered felspar, and *c.* that of the outer layer, both dried at 100° C.

The artificial clay so produced, when examined with high powers under the microscope, exactly resembled ordinary well-prepared kaolin. It was entirely free from hexagonal scales, but contained a number of minute colourless cubes, which were probably fluor-spar.

5. *Conclusion.*—It seems to me that this series of experiments and results, taken in conjunction with the facts which I have cited, is quite sufficient to show that the hypothesis of carbonic acid, acting from below, for ordinary kaolin districts, is untenable, particularly as it does not in any way account for the universal presence of minerals of secondary origin containing fluorine, nor for the frequent occurrence of tin-oxide. There is still more reason for rejecting the hypothesis of carbonic acid

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[1] Communicated to the Royal Institution of Cornwall some years since

acting from above. Whether as a constituent of the atmosphere or as a solution in water, it cannot have produced veins and bands of carclazyte extending far below the drainage-level of the country. As regards the kaolinisation of felspathic rocks *in situ,* I believe that the hypothetical conclusions of Von Buch and Daubrée are worthy of general acceptance.

Derivative clay-beds are of course formed to some extent by the subaerial denudation of carclazyte and kindred rock-masses—already kaolinised. Apart from such masses, however, it is highly probable that the carbonic acid of the atmosphere plays a great part in the production of derivative clays by chemically acting on the surfaces of felspathic and other rock-silicates, and so assisting mechanical action, frost and other denuding agents: also by converting abraded particles of such rocks into kaolin.