

Clay derived from sillimanite by hydrothermal alteration

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THE association of clay minerals with sillimanite near Williams-town, approximately 23 miles north-east of Adelaide, South Australia, has been noted by the writer in earlier papers (Alderman, 1942, 1950). These papers described the occurrence of quartz-sillimanite and quartz-kyanite rocks and gave the evidences which suggest that they were formed metasomatically by alumina-rich fluids at high temperatures. It was also suggested that as the alumina-concentration and temperature of the fluids decreased the metasomatic activity was followed by a period of pegmatite formation which, in turn, gave way to a hydrothermal stage. Brief reference was made to the conversion of sillimanite to clay by hydrothermal agencies.

The clay is well exposed and has been mined for many years as it has excellent refractory qualities. Irregularly distributed throughout the comparatively soft clay material are discrete masses of extremely hard sillimanite-quartz-rutile rock. These are of very variable size and may measure up to several feet in diameter. In the course of mining operations the clay is separated from the sillimanite masses which are also a source of refractory materials.

The textural similarity of freshly broken surfaces of the clay and sillimanite rock as well as their relationship in the deposit strongly suggest that the clay has been formed by alteration of the sillimanite. This contention is thoroughly confirmed by more precise methods of examination, as will be described later in this paper.

Conversion of sillimanite to clay seems to have taken place along certain definite 'pipes' or channels. Even in such channels the alteration was not by any means complete, as the large masses of quartz-sillimanite rock are almost certainly residuals which have escaped conversion. Also, as described in more detail later, the clay itself always contains a considerable amount of fine unaltered sillimanite. Away from

the areas of alteration quartz-sillimanite rock occurs in massive form and is not associated with clay.

Sillimanite rocks.

In hand-specimens the sillimanite rocks are generally white, flecked with red rutile, and their uniformly fibrous texture gives them a most unusual degree of toughness. In general they can be referred to as quartz-sillimanite-rutile rocks in which the relative amounts of the three components vary widely. In some specimens the volume-percentage of sillimanite may be as high as 98 %, in others quartz is the most plentiful component. Rutile contents up to 3 % are quite usual. Varying but generally small amounts of clay mineral are present in the sillimanite masses which are obtained from the clay mines. Occasional grains of kyanite and its alteration product, damourite, frequently occur in association with quartz veinlets. The more quartzose varieties often show a rough banding in which quartz-rich bands alternate with bands richer in sillimanite.

A typical analysis of quartz-sillimanite-rutile rock is ('Mining Review', 1940): SiO₂ 41.26; TiO₂ 2.70; Al₂O₃ 54.35; Fe₂O₃ 0.59; FeO n.d.; MgO 0.08; CaO 0.44; Na₂O 0.02; K₂O nil; H₂O + 0.40; H₂O - 0.02; CO₂ nil; total 99.86.

The analysis suggests that this sample contained approximately 86 % sillimanite, 9 % quartz, and 2.7 % rutile. One of these rocks which consists almost entirely of finely fibrous sillimanite is illustrated in fig. 1.

Clay rocks.

The outstanding feature of the clay rocks is the invariable presence of a considerable proportion of sillimanite. This occurs as fine needles and groups of fibres which have escaped hydrothermal alteration to clay. The fibres vary in length from several millimetres down to two or three microns. The size of the smallest fibres makes both the complete separation of sillimanite from clay and a satisfactory determination of the relative amounts of these two components matters of great practical difficulty.

The clay component proves to be kaolinite, although there are certain indications that a small proportion of dickite may also be present. Rutile has a distribution similar to that in the original sillimanite rock. The proportion of quartz is variable, as it is in the sillimanite rocks, and the matter remains uncertain as to whether it has increased or decreased as a result of the hydrothermal activity. A small amount of diasporite is

present in some samples and is presumably a by-product in the conversion of sillimanite to clay. Also present are irregularly distributed



FIG. 1. Thin section of unaltered sillimanite rock. The whole of the field is occupied by uniformly fibrous sillimanite. Parallel nicols, $\times 52$.

amounts of damourite derived from the alteration of kyanite, relics of which can also be recognized in some samples.

Typical analyses of clay rocks are (Jack, 1926):

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O
1 ...	44.04	0.52	44.74	0.29	n.d.	nil.	0.32	0.39
2 ...	42.86	0.04	47.96	0.30	n.d.	0.12	0.04	0.18
	K ₂ O	H ₂ O +	H ₂ O -	CO ₂	Cl	Total		
1 ...	0.19	9.10	1.00	nil.	0.04	100.63		
2 ...	0.41	8.00	0.60	nil.	0.01	100.52		

Considering only the four main mineral components these analyses suggest that the approximate compositions of these samples were (1) kaolinite 65 %, sillimanite 30 %, quartz 3 %, rutile 0.5 %; (2) kaolinite 57 %, sillimanite 40 %, quartz 1 %, rutile trace. Despite the limitations of such calculations these figures seem to give a reasonable estimate of the actual proportions of minerals present in samples typical of the material mined for refractory clay.

Microscopic examination of thin sections of the clay rocks gives a very clear picture of the alteration of sillimanite to clay. The hydrothermal

fluids seem to have worked their way between the sillimanite fibres as well as across the fibres following lines of transverse fracture. This dismembering of the sillimanite aggregates is accompanied by a lowering of birefringence and eventually by complete breakdown into finely granular aggregates of clay. The reproduced photograph (fig. 2) illustrates these features.

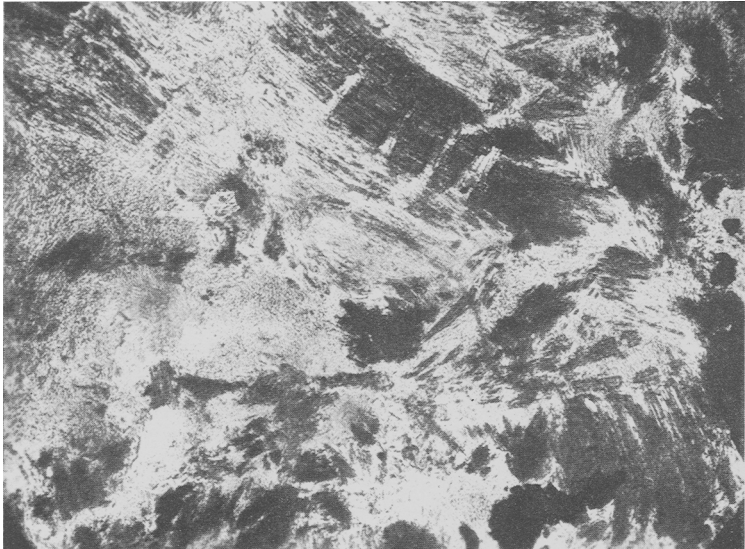


FIG. 2. Thin section of clay rock. Dark areas are mainly sillimanite, light areas mainly kaolinite. The large sillimanite aggregates show alteration to kaolinite parallel to the fibres and along lines of transverse fracture. Ordinary light, $\times 52$.

Narrow shear-zones in the clay rocks are filled with remarkably pure kaolinite. The movement in these shears must have been small although the surfaces of the clay show well-developed slickensides. It is uncertain whether the movement caused mechanical segregation of kaolinite into narrow veins or whether the kaolinite was deposited from solution into earlier-formed fissures. Small areas in these veins consist of kaolinite alone, although most specimens also contain small amounts of sillimanite and quartz which, however, are in much smaller proportion than in the massive clay rocks.

Clay mineralogy.

In thin section the clay mineral is colourless and, as is usual, too fine-grained to allow satisfactory determination by optical methods.

Some flakes which were larger than the average appeared to show a positive optical character which suggested that the mineral was dickite rather than kaolinite. However, staining methods, X-ray examination, dehydration curves, and electron microscopy all indicate that the bulk

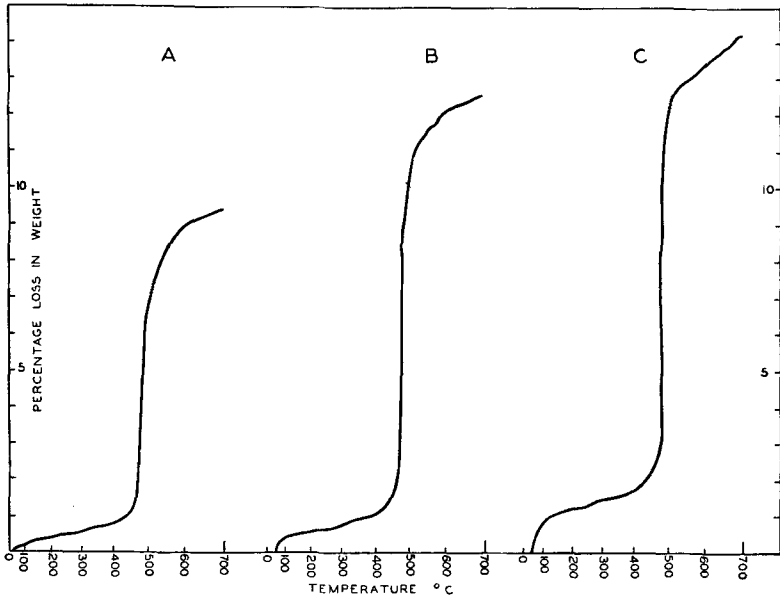


FIG. 3. Dehydration curves of:—*A*. Fine fraction from massive clay rocks, Williamstown. *B*. Kaolinite from shear-zone, Williamstown. *C*. Kaolinite, Cromer ('Cromer C' clay).

of the clay mineral is kaolinite while allowing the possibility, or giving some indication, that a small proportion of dickite is also present. Some of the larger and more flaky fragments do not, for instance, become stained by methylene blue to the same extent as the bulk of the finer clay. X-ray powder photographs, as made and commented on by Dr. A. L. G. Rees, indicate that the clay is largely kaolinite, although the relative intensity of the 1.79 Å. reflection suggests the presence of some dickite.

The dehydration curves (fig. 3) were made by Mr. A. J. Gaskin using a controlled, self-recording dehydration apparatus which he has developed. Of the three curves shown in the diagram curve *A* represents the fine fraction of the massive Williamstown material. The low total-water loss shown by this curve indicates that the sample contained a considerable proportion of non-hydrated mineral, which in this fraction

would be almost entirely sillimanite. The proportion of water lost in the range 500–600° C. is appreciably greater than would be expected from a 'pure' kaolinite. This favours the suggested presence of some dickite which loses most of its water at about 540° C. (Ross and Kerr, 1930). However, the main water loss of this sample takes place at a little less than 500° C. which is normal for kaolinite.

Curve *B* represents clay from the same deposit but from the shear zones which have been referred to above. The proportion of non-hydrated impurity in this sample is much lower than that from the massive clay represented by curve *A*. The curve indicates a fairly pure kaolinite.

Curve *C* is included for purposes of comparison. It represents a reasonably pure kaolinite from Cromer, a deposit in the same district but of entirely different origin. The Cromer clay was derived from hydrothermal alteration of pegmatitic felspar and has no connexion with the sillimanite rocks of Williamstown.

The electron micrograph (fig. 4) illustrates a fine fraction of the normal Williamstown clay. Kaolinite, showing typical outlines, constitutes the bulk of the material. The long narrow aggregate is assumed to be a fibre of sillimanite, which is known to be present even in these fine-grained fractions, and gives striking evidence of the difficulties of making a clean separation of the clay minerals.

Discussion.

The point of greatest interest in the Williamstown kaolinite is its derivation from sillimanite. As far as the writer is aware no similar occurrence has previously been described, although Dr. H. von Ecker-mann has mentioned (Alderman, 1948, discussion) that in the migmatites around the Alnö alkaline intrusion sillimanite is altered to montmorillonite.

It has been suggested in more detail elsewhere (Alderman, 1942, 1948) that the quartz-kyanite and quartz-sillimanite rocks owed their origin to metasomatic agencies in which alumina-containing fluids of high concentration and at elevated temperature reacted with various members of a series of pre-Cambrian schists. As the temperature and alumina-concentration became lower a pegmatite phase ensued in which quartz-kyanite-oligoclase-pegmatites were formed and were followed later by normal quartz-orthoclase-mica-pegmatites. By the end of the pegmatitic phase the active fluids apparently consisted largely of water with silica and some potassium. The reactions produced by these

fluids can best be described as hydrothermal. The earlier-formed kyanite and sillimanite were unstable under these hydrothermal conditions, kyanite being altered to damourite and sillimanite to clay.

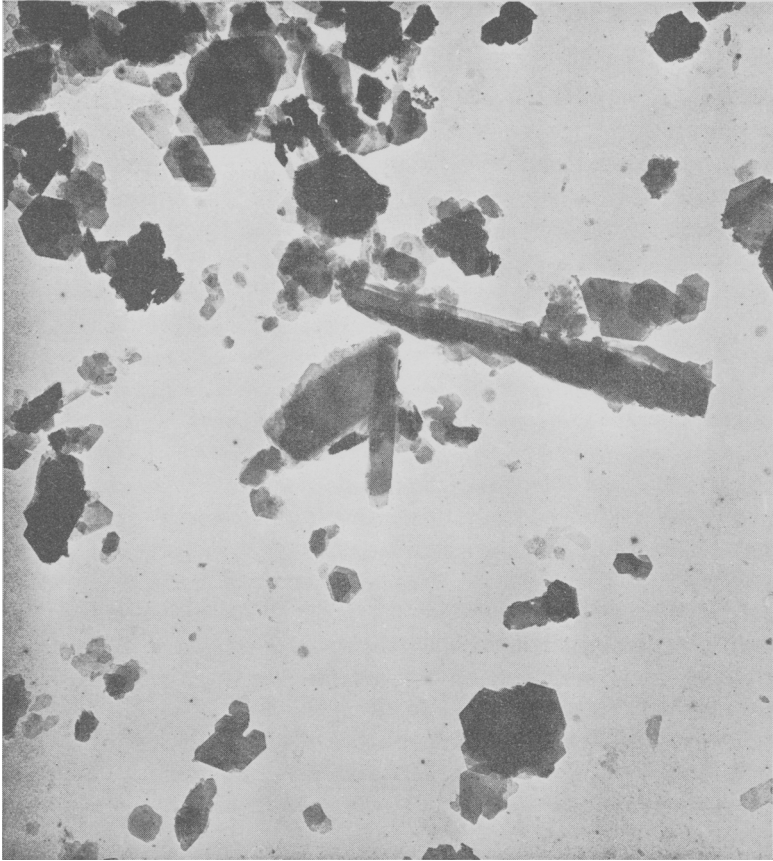
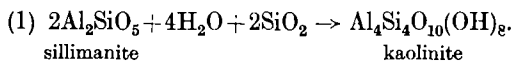


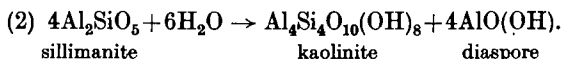
FIG. 4. Electron micrograph of fine fraction of Williamstown clay. Most grains show typical kaolinite outlines. The long aggregate is assumed to be a fibre of sillimanite. $\times 15,000$.

The reactions involved in the kaolinization of sillimanite appear to be simple and in a general way can be represented by the equation:



This equation assumes that there was sufficient silica in the hydrothermal fluids, or made available from quartz in the adjacent rock, to

convert sillimanite completely to kaolinite. This, however, could not have been entirely so, as a small amount of diaspore is distributed throughout the clay rocks. It is suggested therefore that to some extent the reaction may have followed that given in equation:



The reaction given in equation (1) was probably much the greater factor in the process of kaolinization. The extent to which the silica involved in this reaction was derived from quartz in the sillimanite rocks is uncertain. The quartz-sillimanite ratio in these rocks is almost infinitely variable and it is generally impossible to judge the original quartz-content of any of the present clay rocks. However, some unaltered sillimanite rocks contain very little quartz, and representatives of this sillimanite-rich type have apparently become kaolinized. As the diaspore content of these rocks is very small, it would appear that the hydrothermal fluids must have contained very nearly enough silica to effect the reaction suggested by equation (1) without the help of silica from adjacent quartz.

The conversion of kyanite to damourite seems to have been analogous to the kaolinization of the sillimanite but involves the presence of potassium. The hydrothermal fluids thus apparently consisted very largely of water and silica with some potassium, a composition which can be considered as quite normal. Field evidences concerning the temperature at which these fluids were active are obscure.

Experimental work designed to investigate these changes is at present in progress. It has advanced far enough to indicate, even in the very limited range of conditions so far examined, that hydrothermal change in sillimanite can be induced in the laboratory. The work has, however, not progressed sufficiently to allow any certain identification of the phase changes.

Acknowledgements.

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