CHAPTER I

INTRODUCTION. THE CHEMICAL AND PHYSICAL PROPERTIES OF CLAY

The chief uses of clay have been recognized since the earliest periods of civilization; the ancient Assyrian and Egyptian records contain numerous references to the employment of clay for the manufacture of bricks and for fulling or whitening cloth.

Clays are distributed so widely and in many cases are so readily accessible that their existence and some of their characteristics are known in entirely uncivilized regions. The use of certain white clays as a food, or at any rate as a means of staving off hunger, is common among some tribes of very primitive peoples. The more important uses of clays for building and other purposes are naturally confined to the more civilized nations.

The term *clay* (A.S. *cloeg*; Welsh *clai*; Dutch *kley*) although used in a scientific sense to include a variety of argillaceous earths (Fr. *argile* = clay) used in the manufacture of bricks, tiles, pottery and ceramic products (Gr. *keramos* = potter's earth) generally, is really a word of popular origin and use. Consequently, it is necessary to bear in mind, when considering geological or other problems of a scientific nature, that this term has been incorporated into scientific terminology and that its use in this connection not infrequently leads to confusion. In short, whilst almost every dictionary includes one or more definitions of clay, and most text-books on geology, mineralogy, and allied sciences either attempt a definition or assume the reader's knowledge of one, there is no entirely satisfactory limitation in regard to the substances which may or may not be included under the term.

Clay is a popular term for a variety of substances of very varied origins, of great dissimilarity in their composition and in many of their chemical and physical properties, and differing greatly in almost every conceivable respect. It is commonly supposed that all clays are plastic, but some of the purest china clays are almost devoid of this property and some of the most impure earths used for brick-making possess it in a striking degree. Shales, on the one hand —whilst clearly a variety of clay—are hard and rock-like, requiring to be reduced to powder and very thoroughly mixed with water before they become plastic; many impure surface deposits, on the other hand, are so highly plastic as to necessitate the addition of other (sandy) materials before they can be used for the manufacture of bricks and tiles.

Attempts have been made to include in the term clay 'all minerals capable of becoming plastic when moistened or mixed with a suitable quantity of water,' but this definition is so wide as to be almost impracticable, and leads to the inclusion of many substances which have no real connection with clays. The limitation of the use of the word 'clay' to the plastic or potentially plastic materials of any single geological epoch is also impracticable, for clays appear to have been deposited in almost every geological period, though there is some difference of opinion as to the time of the formation of certain clays known as *kaolins*.

Clay is not infrequently termed a *mineral*, but this does not apply at all accurately to the many varieties of earths known as 'common clays,' which, together with the 'boulder clays,' contain many minerals and so cannot, as a whole, be included under this term.

Whatever may be the legal significance of the term 'mineral'—which has an important economic bearing on account of minerals being taxed or 'reserved' in some instances where non-minerals (including brick clay) are exempt—there can be no doubt that, scientifically, clay is *not a mineral but a rock*. Whatever mineral (if any) may give the chief characteristic property to the clays as a class must be designated by a special title, for the general term 'clay' will not serve for this purpose. Geologically, the clays are sedimentary rocks, some being unaltered, whilst others—the slates—are notably metamorphosed and can seldom be used for the purposes for which clays are employed.

Most clays may be regarded as a mixture of quartz grains, undecomposed rock débris and various decomposition products of rocks; if the last-named consists chiefly of certain hydrous alumino-silicates, they may be termed 'clay substance' (see Chapter VI). The imperfections of this statement as a definition are obvious when it is remembered that it may include a mixture of fine sand and clay containing only 30 per cent. of the latter substance.

It is, at the present time, quite impossible to construct an accurate definition of the term 'clay.' The most satisfactory hitherto published defines 'clay' as 'a solid rock composed mainly of hydro-alumino-silicates or alumino-silicic acids, but often containing large proportions of other materials; the whole possessing the property of becoming plastic when treated with water, and of hardening to a stone-like mass when heated to redness.'

From what has already been written, it will be understood that there is no such entity as a standard clay, for the varieties are almost endless, and the differences between them are sometimes so slight as to be scarcely distinguishable.

A further consideration of this branch of the subject may, however, conveniently be deferred to a subsequent chapter.

The best-known clays are the surface clays, loams and marls, the shales and other sub-surface clays, and the pottery and china clays. The values of these different materials vary enormously, some being almost worthless whilst others are highly valued.

The *surface clays* are chiefly used for the manufacture of bricks and tiles (though some are quite unsuitable for this purpose) and form the soil employed in agriculture in many districts.

The *sub-surface clays* and *shales* are harder, and usually require mechanical treatment before they can be used for brick and terra-cotta manufacture, or for the production of refractory and sanitary articles.

The *pottery and china clays* are usually more free from accessory constituents, and are regarded as the 'purest' clays on the market, though a considerable amount of latitude must be allowed in interpreting the term 'pure.' China clays are by no means pure in the state in which they occur, and require careful treatment before they can be sold.

Further information with regard to the characteristics of certain clays will be found in Chapter V.

THE CHEMICAL PROPERTIES OF CLAY.

The chief constituents of all clays are alumina and silica, the latter being always in excess of the former. These two oxides are, apparently, combined to form a hydro-alumino-silicate or alumino-silicic acid corresponding to the formula $H_4Al_2Si_2O_9$[1], but many clays contain a much larger proportion of silica than is required to form this compound, and other alumino-silicates also occur in them in varying proportions (see Chapters V and VI).

All clays may, apparently, be regarded as consisting of a mixture of one or more hydrous alumino-silicates with free silica and other non-plastic minerals or rock granules, and their chemical properties are largely dependent on the nature and proportion of these accessory ingredients.

The purest forms of clay (china clays and ball clays) approximate to the formula above-mentioned, but others differ widely from it, as will be seen from the analyses on p. 16. The chemical properties of pure clay are described more fully in Chapter VI.

[1] This formula is commonly written $Al_2O_3 2SiO_2 2H_2O$, but although this is a convenient arrangement, it must not be understood to mean that clays contain water in a state of combination similar to that in such substances as washing soda—$Na_2CO_3 24H_2O$, or zinc sulphate crystals—$ZnSO_4 7H_2O$ (see Chapter VI).

Taking china clay, which has been carefully purified by levigation, as representative of the composition of a 'pure' clay, it will be found that the chief impurities in clays are (*a*) stones, gravel and sand—removable by washing or sifting; (*b*) felspar, mica and other silicates and free silica—which cannot be completely removed without affecting the clay and (*c*) lime, magnesia, iron, potash and soda compounds, together with minute quantities of other oxides, all of which appear to be so closely connected with the clay as to be incapable of removal from it by any mechanical methods of purification.

To give a detailed description of the effect of each of the impurities just referred to would necessitate a much larger volume than the present, but a few brief notes on the more important ones are essential to a further consideration of the natural history of clay.

Stones, gravel and *sand* are most noticeable in the boulder clays, but they occur in clays of most geological ages, though in very varying proportions. Sometimes the stones are so large that they may be readily picked out by hand; in any case the stones, gravel and most of the sand may be removed by mixing the material with a sufficient quantity of water and passing the 'slip' through a fine sieve, or by allowing it to remain stationary for a few moments and then allowing the supernatant liquid to run off into a settling tank. Some clays contain sand grains which are so fine that they cannot be removed in this manner and the clay must then be washed out by a stream of water with a velocity not exceeding 2 ft. per hour. Even then, the clay so removed may be found to contain minute grains of silt, much of which may be removed by a series of sedimentations for various periods, though a material perfectly free from non-plastic granules may be unattainable.

Most of the sand found associated with clays is in the form of fragments of *quartz* crystals (fig. 1), though it may be composed of irregular particles of other minerals or of amorphous silica.

Felspar, *mica* and other adventitious silicates occur in many natural clays in so fine a state of division that their removal would be unremunerative. In addition to this they act as fluxes when the clays are heated in kilns, binding the less fusible particles together and forming a far stronger mass than would otherwise be produced. Consequently, they are valuable constituents in clays used for the manufacture of articles in which strength or imperviousness is important. If these minerals are present in the form of particles which are sufficiently large to be removed by elutriation in the manner described on the previous page, the purification of the clay is not difficult. Usually, however, the most careful treatment fails to remove all these minerals; their presence may then be detected by microscopical examination and by chemical analysis. For most of the purposes for which clays are used, small proportions of these

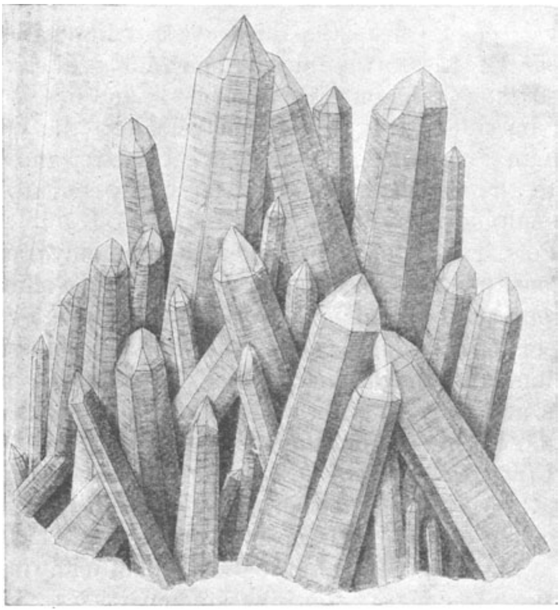

Fig. 1. Quartz crystals, natural size. (*From Miers'* Mineralogy *by permission of Macmillan & Co.*)

silicates are unimportant, but where clays of a highly refractory nature are required; and for most of the purposes for which china clays (kaolins) are employed, they must not be present to the extent of more than 5 per cent., smaller proportions being preferable.

Oxides, sulphides, sulphates and *carbonates* of various metals form the third class of impurities in clays. Of these, the most important are calcium oxide (lime), calcium carbonate (chalk and limestone), calcium sulphate (gypsum and selenite), the corresponding magnesia, magnesium carbonate, and sulphate, the various iron oxides, ferrous carbonate and iron sulphides (pyrite and marcasite) (p. 13).

Potash and soda compounds are commonly present as consituents of the felspar, mica, or other silicates present, and need no further description, though small proportions of *soluble salts*—chiefly sodium, potassium, calcium and magnesium sulphates—occur in most clays and may cause a white scum on bricks and terra-cotta made from them.

Lime and magnesia compounds may occur as silicates (varieties of felspar, mica, etc.), but their most important occurrence is as chalk or limestone. *Chalk* is a constant constituent of malms[1] and of many marls, but the latter may contain limestone particles. *Limestone* occurs in many marls and to a smaller extent in other clays. In the boulder clays it frequently forms a large portion of the stony material. If the grains are very small (as in chalk), the lime compounds

[1] A *malm* is a natural mixture of clay and chalk (p. 68).