

# Process Mineralogy of Ceramic Materials

Edited by

Wolfgang Baumgart

A.C. Dunham

G. Christian Amstutz



 Enke

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With the collaboration of

J. Estel, U. Keppler, D. Knöfel, H.-J. Krause,

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# Preface

When working with ceramic materials the editors had felt for many years that there was a gap in the available literature particularly amongst existing textbooks and monographs. It is, therefore, the aim of this book to fill this gap. It is directed at all those active in the application of, and in research on, ceramic materials in manufacture and use.

Obviously, those active in these fields will come from a variety of disciplines; from the mineralogical, the ceramic, the metallurgical side, or from the materials engineering and allied fields. Among these professionals the book directs itself mainly at the advanced student or the young scientist and engineer, at the stage when he has acquired a basic knowledge of methods in mineralogical analysis, including not only optical methods, but all other common modern analytical techniques (X-ray analysis, various spectroscopic methods, microprobe analysis, etc.).

The editors hope that this book will prove useful in both teaching and research, and that it will be used as an advanced textbook of the applied mineralogy of mineralogical ceramics. Naturally, the individual articles are compact, but exhaustive treatments of the subject matter was not possible. Instead, the chapters are meant to be introductions to the subjects and the reader is referred to the listed literature for more information, and also to standard periodicals and abstract journals (Ceramic Abstracts, Chemical Abstracts, Mineralogical Abstracts, the Industrial Arts Index, and other standard index and abstract journals).

Each of the chapters of this book is written by specialists in the specific fields, active either in industry or in education, or in both. It is truly a cooperative text, reflecting joint work between various fields of the natural sciences and technology, especially physics, chemistry, physical chemistry, and the material sciences.

The editors hope in particular that the book will serve as a bridge for many students into the fields of industrial applications. Process Mineralogy is defined as the application of the methods of mineralogical solid state testing or analysis. Accordingly, a definition of the International Committee on Applied Mineralogy reads as follows:

“Applied Mineralogy covers the complete spectrum of mineralogical activity in the exploration for, and exploitation of, base metals, base minerals, industrial minerals, building and construction minerals, and carbonaceous materials, in mining, extractive metallurgy, and economic geology, as well as in the investigation and development of refractories, ceramics, cements, alloys, and other industrial materials.”

The present book, of course, restricts itself to ceramic materials as understood in the broadest sense. However, a few allied fields are not included, e.g. surface protection problems, archaeological ceramics, zeolites, enamels, nuclear plant materials.

The editors wish to acknowledge the smooth cooperation of the authors who were willing to condense their vast material into the narrow limits of a summary article. Since English is not the native language of the authors, one of the editors (A.C.D.) was kind enough to undertake the chore of correcting the texts. The publisher was also very cooperative and patient in the overcoming of various organizational hurdles and timing problems.



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# 1 Silicate Ceramics

by K.H. SCHÜLLER

## 1.1 Definitions

The term "ceramics" is used in a different way in different countries. In America, the term ceramics covers the total field of inorganic non-metallic materials including whitewares, structural clay products, refractories, oxide ceramics, non-oxide ceramics, glass and glass ceramics, porcelain, enamels, cement and concrete, lime, gypsum, slags, foundry sand, abrasives, and single crystals. In Continental Europe, the meaning of ceramics is more restricted; according to a definition given by DIETZEL (1964) it covers inorganic, non-metallic materials mainly of crystalline nature, insoluble in water and formed by heating to high temperatures during production or use.

Another definition relates to ceramic technology: the study of ceramics is defined as the science of materials which are worked in a plastic state and will develop a rigid structure after firing. Other materials are produced differently, for example, by melting and crystallization. Ceramic materials can also be grouped according to the properties of the final products. HENNICKE (1967) proposed that the following characteristics be used for further subdivision of ceramic materials:

- The presence of significant amounts of clay in the batch: clay ceramics and special ceramics. The border line is proposed at 20% clay content in the batch.
- The size of homogeneous areas in the structure. If various phases and components are large enough to be distinguished visibly, these materials are considered coarse-grained ceramics. Otherwise, they are termed fine-grained ceramics. The maximum particle size forming a homogeneous area should not exceed 0.1 mm.
- The porosity of the fired materials: porous materials and dense materials. A material is porous when the water absorption exceeds 2% in fine-grained ceramics and 6% in coarse-grained ceramics respectively.
- The colour of the fired body: white ceramics and coloured ceramics.

Using these characteristics the various materials may be classified as shown in Tab. 1.1. This classification is favoured now for the international standardization of ceramic materials.

From the many different fields of ceramics, whitewares and structural clay products are discussed in this chapter, i.e. the ceramic products which are mainly based on clays as raw materials.

## 1.2 Raw Materials

Most of the components used in whitewares and structural clay products are natural raw materials: clays and kaolins, sands, feldspars, carbonates und soapstones. In special products some synthetic raw materials are used, e.g. alumina in special porcelains.

**Table 1.1** Ceramic Materials

Specification	Water Absorption	Types and Examples
<b>1 Silicate ceramics</b>		
1.1 Coarse materials		
1.1.1 Porous materials	> 6%	Bricks, Tiles, Fireclay refractories
1.1.2 Dense materials	< 6%	Clinkers, building ceramics, acid proof refractories
1.2 Fine ceramics		
1.2.1 Porous materials, coloured	> 2%	Pottery, majolica
1.2.2 Porous materials, bright	> 2%	Earthenware
1.2.3 Dense materials, coloured	< 2%	Stoneware, Steatite
1.2.4 Dense materials, white, translucent	< 2%	Porcelain, china
<b>2 Oxide ceramics</b>		
2.1 Coarse materials		
2.1.1 Porous materials	> 4%	Refractories (alumina, magnesia, chromite, zirconia, forsterite, silica)
2.1.2 Dense materials	< 2%	Fused cast refractories, Isostatically pressed refractories
2.2 Fine materials		
2.2.1 Porous materials	< 2%	Grinding wheels, Insulating materials, e.g. from alumina
2.2.2 Dense materials	< 2%	Alumina, Zirconia, Beryllia
<b>3 Non-oxide ceramics</b>		
3.1 Coarse materials	> 4%	Carbon refractories, Silicon carbide refractories
3.2 Fine materials		
3.2.1 Porous materials	< 2%	Reaction bonded silicon nitride, Reaction bonded silicon carbide
3.2.2 Dense materials	< 2%	Hot pressed silicon nitride, Hot pressed silicon carbide, Carbon ceramics

## 1.2.1 Clays and Kaolins

### 1.2.1.1 Formation of Clays in Nature

Clays have been formed in nature principally by mechanical and chemical weathering of igneous or metamorphic rocks. The feldspars in these rocks have been disintegrated to clay minerals, mainly kaolinite; under certain conditions montmorillonite is formed giving rise to the formation of bentonites. Micas are occasionally preserved, but generally they are decomposed to hydrous micas, the illites. Quartz is not altered by weathering processes; therefore, it is a common constituent of clays. Thus kaolinite, illite and quartz are the main constituents of clays. Less pure clays like those used in brick fabrication may also contain chlorites and calcite as major constituents.

### 1.2.1.2 Residual and Sedimentary Clays

The clay once formed from the parent rock may be disintegrated in situ or it may be transported by water or wind and redeposited at some distance from its place of origin. In the first case the clay is said to be a residual or primary clay; in the second case it is called a sedimentary or secondary clay.

Sedimentary clays have been naturally processed during transportation. Coarse particles settle quickly. Fine particles are kept in suspension and carried to the final deposit. Therefore, sedimentary clays are usually of finer particle size than residual ones; moreover, the fine particles of the clay minerals are enriched in the sedimentary clays. This results in higher plasticity and dry strength of those clays. However, during transportation the sedimentary clays may have been contaminated by some impurities collected during transportation, e.g. by some iron-bearing minerals or organic matter. The different grain sizes and content of impurities in residual and sedimentary clays govern their properties and thus their different fields of application.

### 1.2.1.3 The Clay Minerals

In mineralogy, the term clay is commonly used to define all sedimentary rocks in which the particles are mainly in the size range below 2 microns regardless of their mineralogical composition. For technical application in ceramics only some clays are of interest; those which have a high amount of special aluminosilicates, the clay minerals.

The structures of these clay minerals are based on the combination or condensation of two different layer structures. One layer, the silica layer or tetrahedral layer, is composed of silicon and oxygen atoms with  $\text{SiO}_4$  tetrahedra forming the layer structure. The second layer, the gibbsite layer, or more generally the octahedral layer, is composed of aluminum and oxygen atoms and hydroxyl groups;  $\text{Al}(\text{O}, \text{OH})_6$  octahedra are the base groups forming the layer structure.

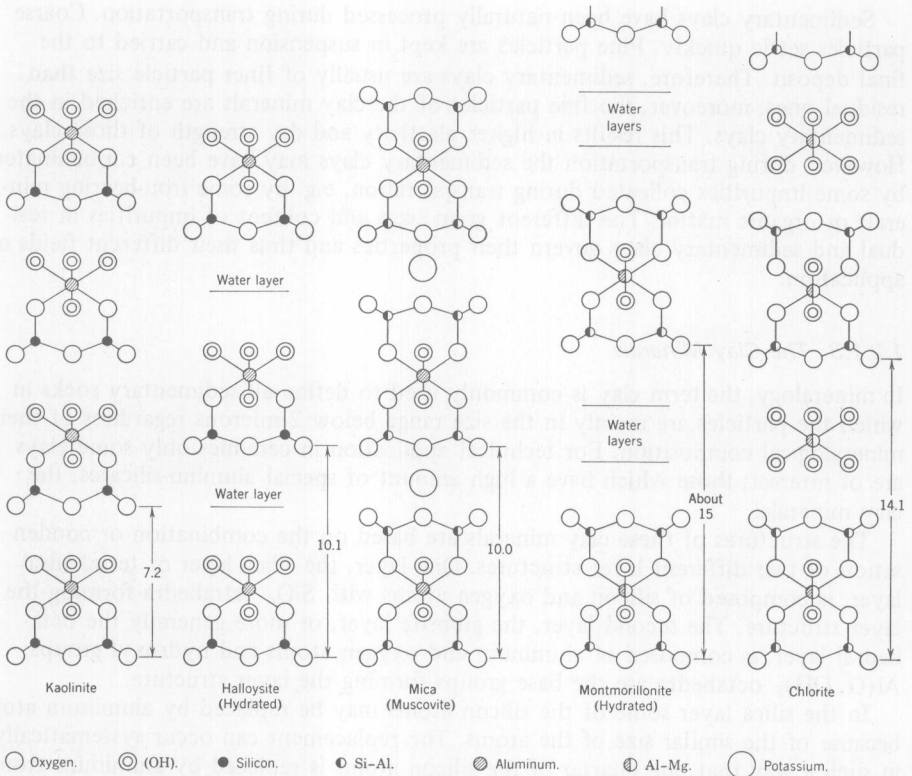
In the silica layer some of the silicon atoms may be replaced by aluminum atoms because of the similar size of the atoms. The replacement can occur systematically, in such a way that one quarter of the silicon atoms is replaced by aluminum atoms, or only a few silicon atoms may be replaced randomly by aluminum atoms. In the first case the deficiency in positive charges is compensated by additional cations strongly attached to the layer structure; alkali ions or alkaline earth ions are the preferred cations introduced into the structure. In the second case the deficiency in positive charges is compensated by cations adsorbed to the layer structure. These cations can be exchanged; they cause the ion exchange capability of clays which is of great importance for certain properties and thus for technical applications.

A further modification of the layer structures is achieved by replacing two aluminum atoms in the octahedral layer by three di-valent atoms, preferably magnesium. If the replacement is complete the gibbsite layer is transformed to a brucite layer. If only some of the aluminum atoms are replaced in this way the deficiency in positive charges can contribute to the cation exchange capability.

The different clay minerals arise from various combinations of the layers described before (Fig. 1.1).

**Kaolinite** is composed of one silica layer and one gibbsite layer in each sheet, resulting in the formula  $\text{Al}_2[\text{Si}_2\text{O}_5(\text{OH})_4]$ . Due to this combination of layers kaolinite is termed a one-to-one, or single layer mineral.

The combination of a silica layer and a gibbsite layer is electrically neutral and all valencies are satisfied. The link between the kaolinite sheets is achieved by van der Waals' forces, supported by hydrogen bonds between the hydroxyl groups in the gibbsite layer and the oxygens in the silica layer of the neighbouring kaolinite sheet. A number of kaolinite sheets are stacked together in this way, forming hexagonal platelets which are typical of kaolinite (Fig. 1.2).



**Fig. 1.1** Layer structures of various clay minerals (from: G.W. BRINDLEY, *Ion Exchange in Clay Minerals*. In: *Ceramic Fabrication Processes*, W.D. KINGERY [ed.], John Wiley & Sons, New York 1958, pp. 7–23)

**Dickite** and **nackrite** have the same formula and combination of layers like kaolinite; they differ in the mode of stacking of the sheets. Both these minerals are much less common in clays and are therefore of minor interest for a discussion of technically applied clays.

Another mineral of the kaolinite group is **halloysite**, a hydrated type with the formula  $Al_2[Si_2O_5(OH)_4] \cdot 2 H_2O$ . The sheets are curved because of a small difference in the bonding length in the silica and gibbsite layers and because of weaker bonds between the sheets as a consequence of the inserted water molecules; therefore, halloysite is characterized by a tube-like crystal habit.

The interlayer water of halloysite is driven off by gentle heating, resulting in the formation of meta-halloysite. Halloysite is a constituent of some china clays and causes an increase in plasticity of those clays.

**Montmorillonite**  $Al_2[Si_4O_{10}(OH)_2]$  is a mineral with a structure composed of one silica layer and two gibbsite layers. Due to this structure it is termed a two-to-one, or double-layer mineral. The ideal formula is realized in the mineral **pyrophyllite**, a mineral occurring in certain metamorphic rocks.