*Robert B. Heimann*

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*To Gabriele whose love, support, and patience were indispensable for creating this text.*

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# Preface

Modern materials science and engineering technology rely on the three principal classes of material, distinguished by their nature of chemical bonding: metals; ceramics and polymers; and the alloys and composites of these materials. The aim of this treatise is to educate not only graduate and doctoral students but also professionals in mineralogy, chemistry, materials science and related disciplines on the subject of ceramics, both traditional and advanced. Hopefully, it will also serve as a primer for more involved studies in ceramic engineering *proper*, and thus lay the foundation for a more detailed knowledge acquisition.

*Ceramics*, by definition, are inorganic, nonmetallic and predominantly polycrystalline materials that may be shaped at room temperature from a variety of raw materials. They obtain their typical properties by sintering at high temperatures. Unlike the German custom of distinguishing between inorganic (poly)crystalline (ceramics *sensu strictu*) and noncrystalline (glasses) materials, the English usage includes glasses in the generic term "ceramics." However, in this treatise the author will follow the German tradition, and consequently glasses and other amorphous materials will be excluded from the discussions. Nonetheless, silicate-based chemically bonded ceramics (CBCs) such as cements/concrete will be included as, with time, they undergo crystallization processes.

*Ceramics* are the oldest man-made materials, dating back to the dawn of human civilization. They possess an overwhelmingly wide variability in terms of their origin, history, utilization, and mechanical, thermal, optical, biological and electronic properties. Traditional ceramics are based almost exclusively on naturally occurring raw materials, most commonly silicaceous minerals such as clays, micas, quartz and feldspars, although for special applications synthetically produced clay minerals may also be utilized. A smattering of other nonsilicate minerals may also be included, such as gibbsite, magnesite, calcite, and dolomite. In contrast to this, advanced ceramics are produced predominantly from chemically synthesized micro- or nanoscaled pure alumina, titania, zirconia, magnesia and other oxides and their compounds, as well as from the carbides and nitrides of silicon, boron and aluminum, and a host of transitional elements. The processing technologies used include the high-temperature transformation of raw materials into desired ceramic bodies, with highly controlled mechanical, thermal, electrical, tribological and optical properties, in addition to the low-temperature hydrolysis

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of calcium silicates and aluminates to synthesize CBCs such as concrete. Hence, the application of ceramics spans the chasm between traditional silicate-based structural materials such as bricks, earthenware, stoneware, porcelain and concrete, and "high-tech" functionally advanced ceramics such as thermal barrier coatings for aerospace gas turbine blades, electrolyte layers for high-temperature solid oxide fuel cells, ferroic ceramics for sensor and actuator applications, diamond single crystals for future carbon-based integrated circuits, and bioconductive monolithic parts and coatings for bone reconstruction and dental and endoprosthetic hip implants.

The aim of this book is to cover pertinent aspects of the processing, structure, technology and properties of classic and advanced ceramic materials, but without claiming to exhaust the topic even remotely in an encyclopedic fashion. Instead, typical examples will be described that stand *pars pro toto* for the totality of ceramic materials in existence today. Consequently, special emphasis is placed on the mineralogy of the materials described, the basic crystallographic aspects of the thermal transformation processes during the firing of natural ceramic raw materials to arrive at traditional structural ceramics, as well as on the general physical principles of functionally advanced ceramics such as zirconia or silicon nitride, the technically important class of ferroic and superconducting ceramic materials on which many modern "high-tech" applications such as sensors and actuators are based, and last – but not least – bioceramics to replace diseased bone and restore lost functions of the human body.

The plethora of excellent books on ceramics produced during the past thirty years have been devoted predominantly to either the fundamentals, to the process technology, or to the engineering applications of their subject matter, while paying considerably less attention to other subjects. Likewise, books on advanced ceramics are generally replete with highly complex solid-state physics that do not always match the level of interest, let alone the comprehension of their intended audience, from areas of mineralogy, chemistry, and materials engineering. Instead, the present book attempts to take a "middle road" between process engineering and solid-state physics approaches by providing a technical (applied) mineralogy approach. The intention is, therefore, to bridge the perceived abyss between the more deductively oriented realm of physics, chemistry and materials science, and the more inductively and empirically oriented realm of the geosciences. As inherent in the role of technical mineralogy, this different approach will combine – in a synergistic manner – the viewpoints and expertise of geosciences and materials science, and will therefore find its main audience among graduate and doctoral students and professionals of mineralogy that, in this context, can be defined as "the materials science of the solid earth."

The text is largely based on a series of lectures given to graduate students of geosciences at Technische Universität Bergakademie Freiberg between 1993 and 2004, to undergraduate and graduate students of physics and chemistry at Chiang Mai University, Chiang Mai, Thailand, and to graduate students of materials science at Chulalongkorn University, Bangkok, Thailand between 1998 and 2001. The subject matter of ceramics – and in particular of advanced ceramics – is a lively area of research and development endeavor, with several thousands of reports made annually among a host of scientific and trade journals. It would be futile to attempt to cover even a small fraction of this trove of information in a single book; hence, what is provided in the following pages is a mere "snapshot" of past and ongoing developments – no more, no less.

Since in the previous paragraphs the viewpoints of technical (applied) mineralogy have been invoked, a general paradigmatic positioning of this specific discipline should be appended here. Research, development and teaching in the field of technical mineralogy provide a modern, tractable bridge between the classical geosciences and modern materials science. Technical (applied) mineralogy can be defined as that discipline of "mineralogical sciences" that studies the mineralogical structure and properties, the technological fundamentals, and the characterization of raw materials, technical products and processes that include the mineralogy of residual and waste product streams, and pertinent environmental issues. Hence, it is positioned at all crossroads of the "modern materials cycle" (Figure P.1). In particular, it assists in the enhancement of traditional materials, and in the development of novel advanced materials.

The arena of activities of technical mineralogists in academia, government, and industry is extremely diverse and includes, but is not limited to:

- The beneficiation of raw materials (ore, industrial minerals, coal, salts, stone, clay).
- The design, development, synthesis, processing, testing and quality management of technical products (ceramics *per se*, glass, cement, construction materials, pigments), including single crystal growth and mass crystallization as well as their characterization with polarization microscopy and X-rays, but also increasingly modern high-resolution analytical surface techniques.
- The control, remediation, and risk analysis of historical and modern tailings of mining, and ore dressing and smelting activities, as well as the development and validation of environmentally safe materials for sound disposal concepts of domestic and industrial wastes, including radioactive matter.
- Environmental activities to foster a sustainable raw materials and energy economy, including the management of minerals that occur as secondary products of industrial processes, such as gypsum derived from flue gas desulfurization, and other residual and waste materials.
- Damage analysis and the restoration of ancient monuments, as well as the determination of provenance, age, type of material, and manufacturing technologies of historical objects of art (archaeometry).

This wide professional range attesting to the heterogeneity of the discipline creates lively interdisciplinary collaboration among neighboring fields of scientific and engineering endeavors. These fields include solid-state chemistry and physics, materials technology and engineering, process engineering, mining, geology and geophysics, geoecology, biology, medicine, environmental sciences, as well

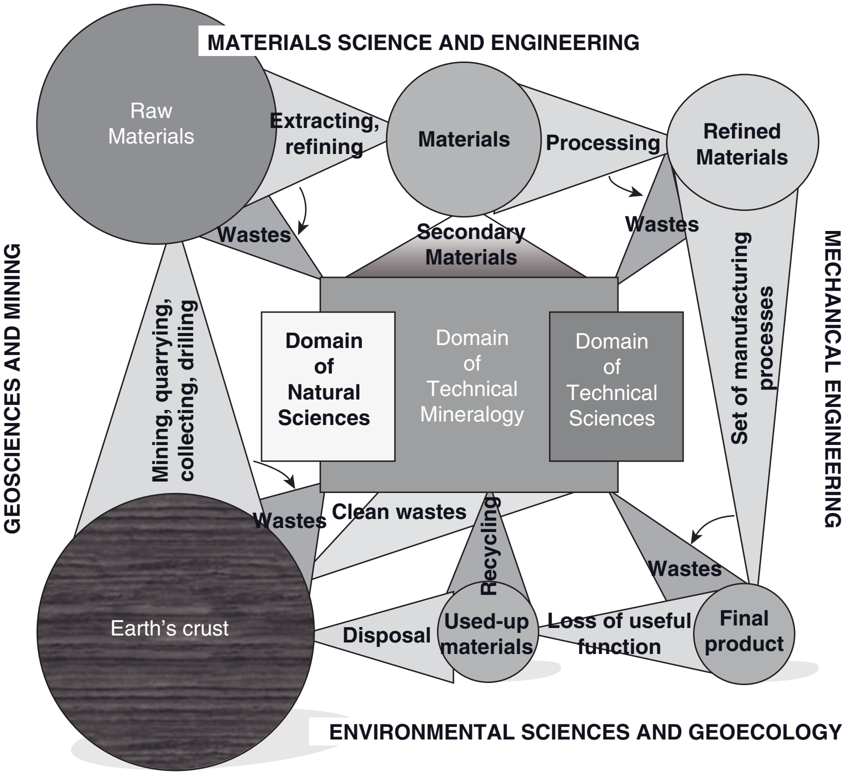

**Figure P.1** The domain of technical mineralogy within the materials cycle. During all operations, from mining to the production of raw and refined materials to the manufacture of end products and to their eventual disposal and/or recycling, several waste material streams are created that challenge R&D in technical (applied) mineralogy. The sizes of the circles symbolize the different relative volumina of the mass streams, whereby the contribution of the Earth's crust is grossly underrepresented.

as archeology and social and cultural sciences. Hence, the curriculum of technical (applied) mineralogy is both versatile and involved. As opposed to chemistry or mechanical engineering, the lack of an industry that directly mirrors the scope of academic research within technical mineralogy somewhat impedes any fruitful research interaction with colleagues in industry. Yet, whilst the variability of the fields of endeavor of technical mineralogy and increasing cross-pollination among neighboring disciplines preclude a clear distinction of responsibilities, the old adage still applies: "Technical mineralogy is what technical mineralogists do."

I am highly indebted to Prof. Dr Dr.h.c. Walter Heywang (München), Prof. Horst J. Pentinghaus (Karlsruhe), Prof. Herbert Pöllmann (Halle) and Dipl.-Phys. Wolfram Wersing (Bergen, Chiemgau) for providing advice and valuable critical comments, and, in particular, to Prof. Hans Hermann Otto (Clausthal-Zellerfeld) for contributing Chapter 9 and Appendix E. The publishing house Wiley-VCH Weinheim, represented by Dr Heike Nöthe, lent important editorial and logistic support.

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*Görlitz*

# 1
# Introduction to Classic Ceramics

## 1.1
## Ceramics through the Ages, and Technological Progress

Throughout the ages of humankind, materials have been the overwhelmingly crucial determinant of the competitiveness of individuals and societies. Today, a better understanding of the atomic and molecular structure of materials is becoming indispensable for the development of new materials, and the improvement of existing materials. As a result, materials are being tailored to meet specific applications to address pressing industrial and societal challenges in the highly competitive contemporary world. In this process, ceramics technology plays a particularly important role, and hence has emerged as a driver of technological progress in many industrial sectors.

It is a widely accepted paradigm that such technological progress takes place in a highly competitive environment where only a limited amount of the required resources exist. Hunger for raw materials has always been a strong driving force in world history. Throughout the history of humankind, the information contained within each newly developed or significantly improved material or technology has increased exponentially. Figure 1.1 suggests that the knowledge required to make pottery – that is, the mining/collecting, processing, forming, and firing of clay, including the knowledge and skill to construct and operate kilns and flues – were orders of magnitude higher than those needed to fashion rather simple tools and implements from bone or stone. The quantification of the “technology information content,” plotted logarithmically on the ordinate of Figure 1.1, is – of course – highly subjective. Nevertheless, it suggests that the knowledge acquired in pottery making has later been put to use to mine, dress, and smelt ore, and to purify and alloy metals. As is evident from the figure, technological development stagnated in the Western societies during the Dark and Middle ages, but eventually took off dramatically during the Renaissance and the emerging Age of Science. Since the rate of change in materials technology is ever-accelerating, the increase in information content – that is, entropy – leads to an ever-decreasing technological half-life of newly invented materials and technologies. The consequences of this effect have been estimated and projected onto future economical and societal trends of developed and developing nations

*Classic and Advanced Ceramics: From Fundamentals to Applications*. Robert B. Heimann

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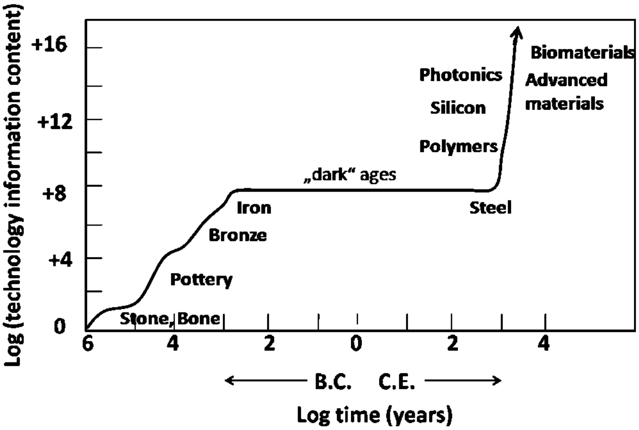

**Figure 1.1** Materials development over time: increase of technology information content. Adapted from Hench (1988).

(see, for example, Hench, 1988; Franklin, 1990; Heimann, 1991; Marchetti, 1997; Heimann, 2004).

The rate of change in the information content of advanced materials duplicates the equally fast rate of information and technology transfer within societies of the developed world (Heimann, 1991). As pointed out by Hench (1988), a positive feedback mode connects the two rates, leading to an autocatalytic relationship between materials and technology. This relationship thrives in technological niches that compete with each other for survival and growth, and is controlled by complicated mechanisms involving small random effects which, however, can accumulate and become magnified by positive feedbacks (Arthur, 1990).

Ceramics *sensu strictu* are the oldest man-made materials. By definition, they are inorganic, nonmetallic, silicate-based materials, insoluble in water and many acids and alkalis, and contain at least 30% crystalline compounds. In general, ceramics are shaped at ambient temperature from a specific raw materials mix by a large variety of forming techniques and tools (see, for example, Brownell, 1976), and obtain their typical properties by firing beyond 800 °C (Hennicke, 1967).

While at the dawn of civilization naturally available "ceramics" such as hard rock and flint were utilized for tools (Figure 1.2), with the advent of fire it became apparent that soft and pliable clay and loam raw materials could eventually be changed into hard, durable shapes that were capable of holding liquids, and consequently these were used as storage containers and cooking pots. This development is thought to have been triggered by the transition from hunter–gatherer to agrarian societies. Through the firing process, clay minerals generated by the weathering of granitic rocks could be transformed back into something resembling an artificial "stone" (Heimann and Franklin, 1979). Later, construction materials such as bricks, tiles, and pipes were produced from fired clay. As early as 1600 B.C., the technology of glazing of bricks was known and exploited by the Babylonians.

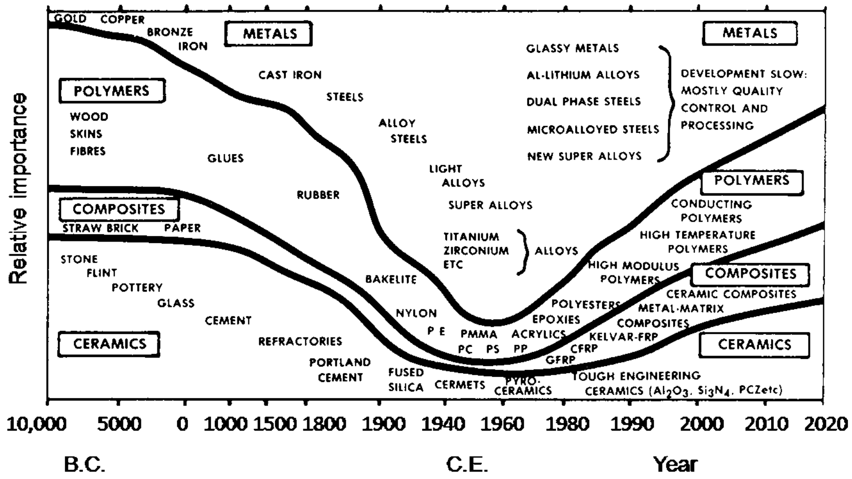

**Figure 1.2** Historical timeline of development of materials (Froes, 1990).

The early history of the ceramic technology is difficult to assess in both geographical and temporal context. Arguably, among the first objects fashioned from clay were maternal goddess images such as the famous Upper Paleolithic "Venus of Dolni Věstonice," Moravia, and fragments of animal and human figurines dating from between 25 000 and 29 000 years ago (Klima, 1962). Near the end of the Mesolithic (13 000–12 000 B.P.), hunter–gatherers living in Japan independently rediscovered ceramic technology, but this time applied it to manufacture the world's oldest known ceramic vessels of the Jōmon culture (Chard, 1974; Sherratt, 1980). Very recently, still earlier remnants of ceramic technology were found in a cave in southern China and dated to between 18 300 and 15 430 cal B.P (Boaretto *et al.*, 2009). Since ceramic shards are well preserved in most soils, they are of overriding importance in archeology to date, and distinguish prehistoric cultures by the unique and enduring physical and stylistic features of their pottery. Highlights in ceramic art and technology are the Greek Attic red-on-black and black-on-red vases of the sixth and fifth centuries B.C., the Roman Terra sigillata ware (first century B.C. to third century C.E.), Chinese Song (960–1279 C.E.) and Ming wares (1368–1644 C.E.), as well as the European developments surrounding the inventions of Faience and Majolica (late fifteenth to early sixteenth century C.E.), soft-paste (Sèvres, France) and triaxial hard-paste (Meissen, Saxony) porcelains of the eighteenth century C.E., and soapstone porcelain and bone china in eighteenth-century England. The art, structure and technology of these ceramics have been magnificently researched and displayed in the seminal work "Ceramic Masterpieces" by Kingery and Vandiver (1986). The British development lines in particular were described by Freestone (1999) and Norton (1978).

In parallel, a second line of development emerged concerned with technical refractory ceramics for applications in ancient metal-working activities, including

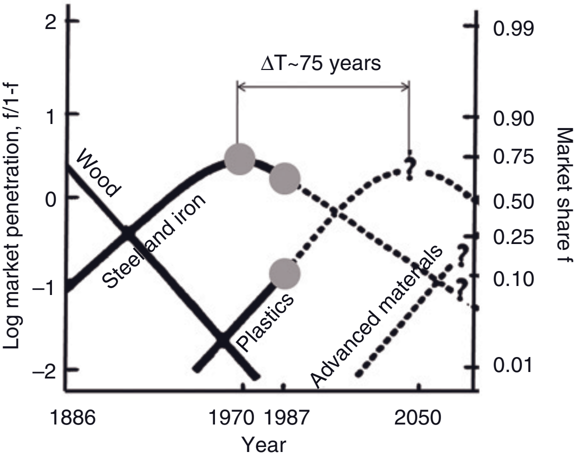

**Figure 1.3** Logistic substitution of structural engineering materials between 1886 and 2050 plotted according to the Marchetti–Nakicenovic model (Marchetti and Nakicenovic 1979; Marchetti, 1997). The maxima of the evolutionary curves are spaced about 75 years apart (i.e., 1.5 times the Kondratieff cycle).

tuyères, kilns, furnace linings, smelting and casting crucibles (Rehren, 1997), glass smelting pots, and saggars for firing delicate – and hence high-priced – pottery (Freestone and Tite, 1986).

As indicated in Figure 1.2, ceramics and ceramics-based composite materials played a very important role during the early technological development period of mankind until about 1500 C.E., when metals technology took over. This lasted until the 1970s, when the ubiquitous application of engineering polymers and their composites reduced the impact of metals (Figure 1.3). However, in parallel a second "ceramic age" emerged, highlighted by the development and practical use of tough engineering, functional, and other advanced ceramics. Today, the production volume of classic ceramics such as bricks, tiles and cement/concrete still drastically outperforms that of advanced ceramics. For example, the present world tonnage of cement produced is in excess of a staggering $2 \times 10^9$ tons annually (see Section 5.2.1). In contrast, the volume of advanced ceramic materials produced is ridiculously small, although owing to their high value-added nature their sales figures approach those of classic ceramics (see Section 6.2).

Around 1970, metal technology – exemplified by the most common construction materials of steel and iron – reached its maximum market penetration of approximately 75%, and then began to decline. Today, these materials are gradually being replaced by engineering plastics, the use of which is predicted to peak around the year 2050. Simultaneously, the use of advanced materials, including advanced ceramics, is on the rise and will presumably reach a market share of about 10% by the year 2050. This model is based on the logistic Volterra–Lotka equation (Prigogine and Stengers, 1984), that is a measure of the continuous competition

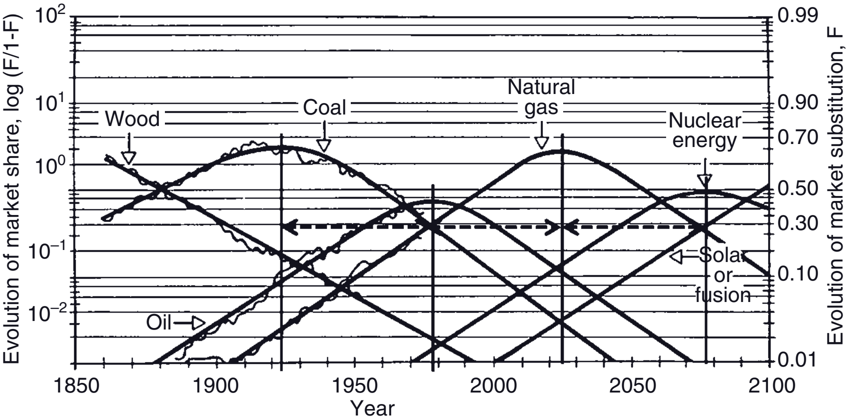

**Figure 1.4** Global use of primary energy sources since 1850 (Marchetti, 1989, 1997). The maxima of the Verhulst logistic curves are spaced 50–55 years apart (Kondratieff cycles). Data beyond 1970 are extrapolated.

of materials and technologies, and the fight for technological niches (Heimann, 1991). The maxima of the overlapping logistic equations (Verhulst equations) are shown to be spaced approximately 75 years apart. This offset, however, does not match the well-known Kondratieff cycle of 50–55 years, which arguably is a series of recurring long-range economic cycles that have been shown to govern numerous evolutionary developments, including discoveries (inventions), innovations,[1] industrial production figures, and primary energy uses (Figure 1.4) (Marchetti, 1981, 1997; see also Heimann, 1991, 2004).

In order to underscore the overriding role that raw materials play in society, two additional scenarios will be juxtaposed: (i) the worldwide industry production; and (ii) the individual use of raw materials per capita and lifetime in present-day Germany. The major growth industries are considered to be energy production and distribution, the chemical industry, and microelectronics. The proportions of these industrial sectors of the total industry production worldwide for 1960 and 1990, and extrapolated to 2025, are shown in Table 1.1. While the energy-producing and chemical industries are assumed to remain constant, microelectronics are predicted to double between 1990 and 2025, whereas the metal-based industries (including processing and machining industries) will show a remarkable decline.

Figure 1.5 lists the tonnage of raw materials used per capita within a person's average lifetime of 70 years in contemporary Germany, representative of the raw materials "hunger" of a developed nation with a high technological and societal efficiency (Millendorfer and Gaspari, 1971; Marchetti, 1981).

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[1] *Innovations* start new industries; *inventions* are discoveries that are at the base of innovations (Marchetti, 1981).

**Table 1.1** Proportion (%) of growth for industries of the total industry production worldwide. Data from United Nations Yearbook (1998).

| Industry | Year | | |
|---|---|---|---|
| | **1960** | **1990** | **2025** |
| Energy | 4.8 | 6.5 | 7.0 |
| Chemistry | 8.5 | 12.9 | 14.0 |
| Microelectronics | 1.9 | 10.3 | **25.0** |
| Metal-based industries | 26.5 | 23.0 | **9.4** |

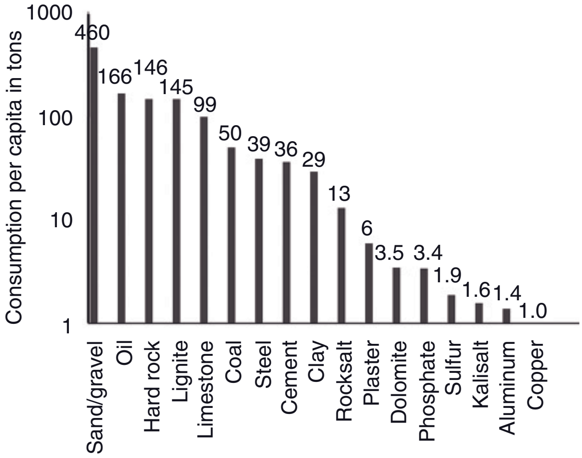

**Figure 1.5** Per capita consumption of material resources in an average lifetime in Germany. Data from Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover, Germany, Global-Report 2859, 1995).

## 1.2
## Classification of Ceramics

A systematic treatment of inorganic–nonmetallic materials is best accomplished by considering a hierarchical approach, as shown in Figure 1.6. The first triangle of level 1 contains the three materials supergroups – metals, polymers, and ceramics – *sensu lato* that are distinguished by their differing chemical bonding relations. The second level of triangles shows at its apices the inorganic–nonmetallic materials classes n that is, ceramics *sensu strictu*, glasses, and hydraulic adhesive materials. These classes can further be subdivided into silicatic, oxidic, and nonoxidic materials (the third hierarchical triangle). Eventually, the chemical components characterize the individual properties (fourth hierarchical triangle). Figure 1.6 is

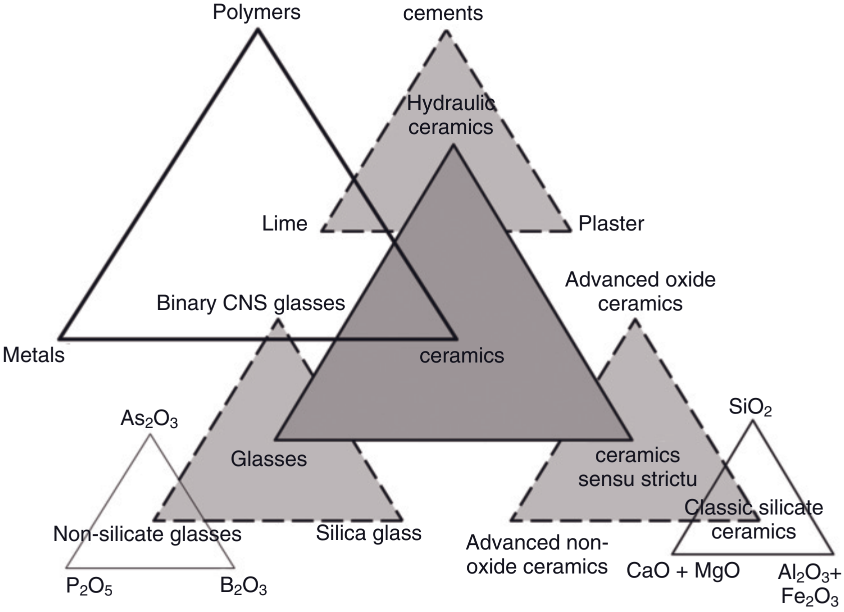

**Figure 1.6** Four levels of hierarchical triangles relating different groups of materials. Level 1 (materials supergroups): metals, polymers, **ceramics**; level 2 (ceramics *sensu lato*): glasses, hydraulic ceramics, **ceramics *sensu strictu***; level 3 (ceramic subgroups): advanced oxide ceramics, advanced non-oxide ceramics, classic silicate ceramics; level 4 (phase diagrams): $SiO_2$, CaO + MgO, $Al_2O_3$ + $Fe_2O_3$.

**Table 1.2** The three main groups of silicatic ceramic materials (level 2 of Figure 1.6).

| Material | Processing steps[a)] | | | $T_{max}$ (°C) | Time of invention |
|---|---|---|---|---|---|
| Ceramics *sensu strictu* | P | F | H | <1450 | <6000 B.C. |
| Glasses | P | H | F | 1500 | <3000 B.C. |
| Cements (CBCs)[b)] | H | P | F | >1500 | Around 1850 |

a) P = powder production; H = heating; F = forming.
b) CBC = chemically bonded ceramic.

intended to show only the principle of the approach; in reality, such a succession of hierarchical triangles would be more complex. For example, the huge variation of chemical compositions inherent in silicate ceramics would require replacing the triangles by higher-dimensional shapes.

The three main groups of ceramics of level 2 are distinguished by their processing temperatures, the succession of processing steps (F = forming, H = heating, P = powder production), and the time of invention (Table 1.2).

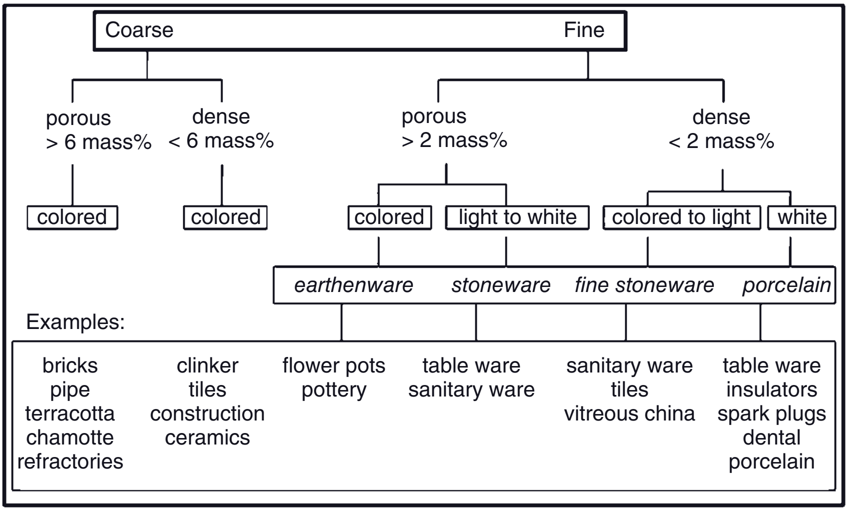

**Figure 1.7** Classification of silicate-based ceramics (after Hennicke, 1967).

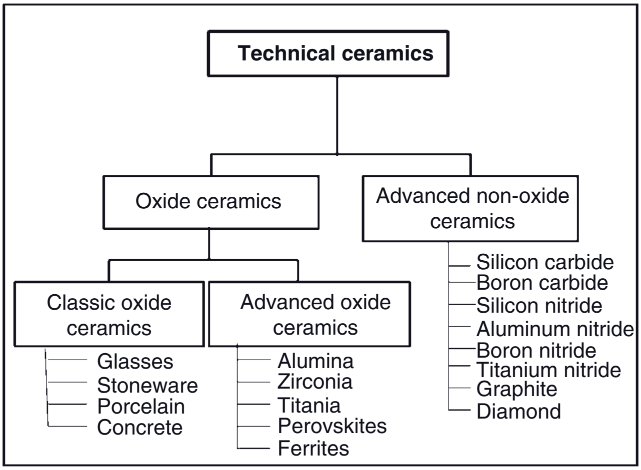

**Figure 1.8** Classification of technical ceramics (level 3 of Figure 1.6).

Historically, silicate-based ceramics have been classified in various ways. One of the most useful schemes (Hennicke, 1967) divides different classic ceramic wares according to their starting powder grain sizes (coarse: >0.1 … 0.2 mm; fine: <0.1 … 0.2 mm), porosity of the fired product, water absorption capacity (<2 … >6 mass%), and color of the fired ceramic body (Figure 1.7).

A classification of the field of technical ceramics is shown in Figure 1.8.

In the chapters following this introduction, the path will be traced from natural silicate-based ceramic raw materials, rheological principles of clay–water interac-