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Review

Principles of demineralization: Modern strategies for the isolation of organic frameworks Part I. Common definitions and history

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Dedicated to Professor Dr. Steve Weiner on the occasion of his 60th birthday.

Abstract

In contrast to biomineralization phenomena, that are among the most widely studied topics in modern material and earth science and biomedicine, much less is systematized on modern view of demineralization. Biomineralized structures and tissues are composites, containing a biologically produced organic matrix and nano- or microscale amorphous or crystalline minerals. Demineralization is the process of removing the inorganic part, or the biominerals, that takes place in nature via either physiological or pathological pathways in organisms. In vitro demineralization processes, used to obtain mechanistic information, consist in the isolation of the mineral phase of the composite biomaterials from the organic matrix. Physiological and pathological demineralization include, for example, bone resorption mediated by osteoclasts. Bioerosion, a more general term for the process of deterioration of the composite biomaterials represents chemical deterioration of the organic and mineral phase followed by biological attack of the composite by microorganisms and enzymes. Bioerosional organisms are represented by endolithic cyanobacteria, fungi, algae, plants, sponges, phoronids and polychaetes, mollusks, fish and echinoids.

In the history of demineralization studies, the driving force was based on problems of human health, mostly dental caries. In this paper we summarize and integrate a number of events, discoveries, milestone papers and books on different aspect of demineralization during the last 400 years. Overall, demineralization is a rapidly growing and challenging aspect of various scientific disciplines such as astrobiology, paleoclimatology, geomedicine, archaeology, geobiology, dentistry, histology, biotechnology, and others to mention just a few.

Keywords: Biomineral; Dissolution; Decalcification; Desilicification; Bioerosion; Remineralization; Dental caries; Bone; Shell; Endoliths; History

Contents

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1. Introduction

This is the first paper from a series on demineralization, and contains common definitions, plus the history of this phenomenon and its practical applications. The next two papers will be dedicated to a detailed analysis of the principles and mechanisms of decalcification (Part II) and desilicification (Part III) relating to naturally occurring composites and artificialy developed biomaterials.

One of the most troublesome points when dealing with demineralization is making a distinction between naturally occurring and in vitro, or laboratory or applied demineralization. One action known as ''quick and deep'' demineralization comes from a chemical point of view where very aggressive chemical reagents have been used, which led to harsh destruction of both mineral and organic phases and to corresponding artifacts. For example, HF-based silica dissolution procedure could drastically change the structure of glass sponge spicular proteins (Croce et al., 2004). As a consequence, when this is the dissolution technique we can learn little about the real nature of the organic matrix of the biomineral or the actions of skeletal formation. The isolation of an organic component from any natural biomineralized material whether mineralized with calcium- or silica-containing compounds is indispensable but in our minds the most efficient and effective technique should be based not on fast dissolution of the inorganic component, but instead on a slow, biomimetically inspired process that would spare the organic component in the biomineral-based naturally occurring composites and not result in artifacts. Therefore we present here a discussion on demineralization as a common phenomenon occurring in nature and compare it to demineralization as a tool that has been widely used in several different practical approaches.

We review the principles and concepts of demineralization and their application in different fields of science, engineering and medicine underscoring the principles and concepts that arise from chemical and biologically mediated perspectives of demineralization. After surveying the major types of biominerals and biocomposites, the common definitions of biomineralization, demineralization and remineralization are discussed, followed by a previously unpublished, detailed description of the history of demineralization including decalcification and desilicification phenomena, which occur in natural environments, in organisms and in the laboratory. The final chapter describes how current knowledge of demineralization is inspiring new directions for practical applications.

2. Biominerals and biomineralization

According to a modern definition (Skinner, 2005) ''a mineral is an element or compound, amorphous or crystalline, formed through biogeochemical processes''. This definition acknowledges that some biominerals are barely crystalline but avoids a discussion of ''amorphous''.

By the 1930s, there were approximately 10 different minerals known to be present in living organisms. This changed when Heinz Lowenstam published a paper (Lowenstam, 1962) describing the presence of magnetite, a relatively hard iron oxide that chemists supposed could only be formed at very high pressures and temperatures. Lowenstam noticed that limestone outcroppings near the ocean shore were being undercut by the scrapping action of chitons, and he went on to show that the surface of the lateral tooth of the chiton radula was covered with magnetite. Since that discovery, numerous biominerals with a range of chemical compositions have been discovered. Most of them are listed in the book by Lowenstam and Weiner (1989).

They list 38 ''common'' minerals found in metazoans; the following cations Ba, Ca, Cu, Fe, K, Mn, Mg, Na, Ni, Pb, Si, Sr, and Zn, occur as hydroxides, oxides, sulfates or sulfides, carbonates and phosphates. Recently, it was reported (Skinner, 2005) that biominerals can be classified in the same framework as minerals, by composition based on the anionic constituents, and that there are representatives in many of the 78 mineral classes listed in Dana's New Mineralogy (Gaines et al., 1997). All biominerals are common minerals, easily accommodated in the usual definition of ''mineral'' but they may have distinct morphologies and certainly do make unique contributions to well-known life forms (Skinner, 2005). Minerals are commonly produced by bacteria, lower and higher plants, and fungi. Among higher phyla most work has been on Cnidaria, Mollusca, Arthropoda, Echinodermata, and Chordata (Wilt, 2005). Further, there are organisms whose hard parts may be formed from one or several of the calcium carbonate polymorphs: calcite, aragonite or vaterite. Moreover, the polymorphs may change between the larval and adult forms (Skinner, 2005).

Biominerals may be deposited within the organism, and within its immediate surroundings or environment, as a result of the metabolism of the living creature (Skinner, 2000).

The variety of biomineralizers can best be expressed by the fact that, approximately 128,000 species of molluscs (Krampitz and Graser, 1988), about 800 species of corals (Frank and Mokady, 2002), 5000 species of sponges including 500 species of glass sponges (Hickman and Roberts, 1994), 700 species of calcareous green, red and brown algae (Dawson, 1966), and more than 300 species of deep-sea benthic foraminifera (Holbourn et al., 2007) exist.

Vertebrate and particularly human biominerals can be divided into two types (Skinner, 2000): those are

1. essential, a normal part of the expected physiology of human systems, such as the mineral matter found in bones (reviewed by Skinner, 2005; Glimcher, 2006; Dorozhkin, 2007) and teeth (reviewed by Robinson et al., 1995; Fincham et al., 1999; Simmer and Hu, 2001).

   There are 208 bones in the skeleton and 32 teeth in the oral cavity of a normal adult (Skinner, 2000) and
2. unexpected, and undesired, or pathologic mineral deposits including
   - pancreatic calculi (Jin et al., 2002) and stones (Multinger et al., 1983);
   - renal stones (Kageyama et al., 2001);
   - kidney stones (Ryall et al., 2000; Khan et al., 2002);

- urinary calculi (Suto and Wooley, 1972), stones (Prien and Prien, 1968; Rose, 1977; Williams et al., 2006) and cystoliths (Saetre, 1954);
- gallstones (Been et al., 1979);
- bladder stones (Chaudhri et al., 2007);
- rhinoliths (calculus present in the nasal cavity) (Rasinger et al., 1985; Cellikkanat et al., 1997; Vink et al., 2002; Shaw, 2007);
- tonsilloliths (oropharyngeal concretions) (Cerny and Bekarek, 1990; Mesolella et al., 2004);
- vaginoliths—vaginal calculi (Malik et al., 2006; Cetinkursun et al., 2001; Malhotra et al., 2004);
- cardiolytes (Gilinskaya et al., 2003);
- cutaneous calculi (Neild and Marsden, 1985; Tezuka, 1980; Moulik et al., 1974);
- enteroliths (Rudge, 1992; Lopez and Welch, 1991; Pantongrag-Brown et al., 1996);
- sialoliths—salivary submandibular (Burstein et al., 1979) and parotid gland stones (Thompson, 1973; Slomiany et al., 1983);
- ptyaliths—calculus in a salivary glands (Anneroth et al., 1975);
- dental calculi (Rabinowitz et al., 1969).

The formation of crystals in pathological mineralization follows the same principles as normal calcifications (Magalhaes et al., 2006).

Biogenic minerals have also been well-documented within the plant kingdom (Franceschi and Horner, 1980; Franceschi and Nakata, 2005). The most common phytocrystals are formed from the calcium oxalate (Cox) hydrates, namely the calcium oxalate monohydrate, and calcium oxalate dihydrate. Typically, Cox crystals appear intracellularly in specialized cells called crystal idioblasts. Extracellulars deposits are a characteristic feature of numerous gymnosperm species and the ontogeny of extracellular deposits in coniferous gymnosperms indicates extracellular origin. However, within Plantae, the carbonate biomineralization of marine and fresh water algae is replaced by silica phytolith mineralization in the epidermis of some vascular plants, especially grasses, sedges, and the sphenosid genus Equisetum (Harrison, 1996; Knoll, 2003).

Another kind of organic–mineral composites discovered in plants is known as cystoliths.

These formations are heavily calcified wall ingrowths that occur in specialized cells called lithocysts in leaves, stems and sometimes roots of species restricted to a few angiosperm families, notably Moraceae, Urticaceae and Acanthaceae (Metcalfe and Chalk, 1983).

Lithocyst are usually localized in the upper and/or lower epidermis, and they are associated with many photosynthetic cells in all plant species investigated, suggesting some relationship between $CaCO_3$ deposition in cystoliths and photosynthesis (Okazaki et al., 1986). The cystolith is a spindle-shaped body composed of concentric layers of longitudinally orientated cellulose microfibrils associated with pectins and other cell wall polysaccharides. At maturity it is heavily impregnated with calcium carbonate (Watt et al., 1987).

Silica-based biocomposites also occur widely in nature. Why some organisms utilize silica rather than calcium carbonate as a structural material is unknown (Mann, 1995). Cell membranes of microorganisms might function as seed crystals for Si precipitation, which is well known from biogeosystems with Si supersaturation, e.g. geothermal springs (Sommer et al., 2006). Due to their small size, bacteria as a group have the highest surface area-to-volume ratio of any group of living organisms and this, together with the presence of charged chemical groups on their cell surface, is responsible for the potent mineral nucleating ability of these cells (Douglas, 2005). Silicic acid which has been taken up from soil solution (actively or passively) is precipitated primarily as amorphous silica at cell walls, lumens, and in the intercellular voids of plants (Ma et al., 2006). Silica-cuticle double layers and silicacellulose double layers were observed on the surface of leaves, stem and hulls (Yoshida, 1965). Some plant cystoliths also contain silicon and are covered in a sheath of siliceous material (Watt et al., 1987). Phytogenic silica in the form of phytoliths is regarded as the major component of the biogenic silica pool in soils, followed by diatoms' skeletons and sponge spicules (Clarke, 2003). Sliceous skeletons and spicules are also known to be present in different Protozoa, e.g. radiolarians (Hertwig, 1879; Cahon and Cahon, 1972), silicoflagellates (Ehrenberg, 1830), sarcodines (Dujardin, 1841). In animals siliceous skeletons are not only limited to glass sponges and demosponges spicules (Uriz, 2006); there are minor occurrences such as the opalized mandibular blades of boreal copepods (Sullivan et al., 1975) and micron-scale silica tablets formed intracellularly in the epidermis of some brachiopod larvae (Williams et al., 2001).

Thus, many biomineralized tissues are composite materials, containing a biologically produced organic matrix and nano- or microscale amorphous or crystalline minerals (De Stasio et al., 2005). During the processes of biomineralization the organic material acts variously as nucleator, cooperative modifier, and matrix or mold for the mineral ions. The resulting tissue has properties very different from those of the pure minerals themselves. The stiff mineral prevents the organic matrix (proteins, peptides, polysaccharides, lipids) from yielding, while the organic matrix prevents the mineral from cracking (Treccani et al., 2003).

Based on the highly regulated biological environments, biomineralization can be classified as an intracellular, intercellular, or extracellular process (Subburaman et al., 2006).

An understanding of how organisms select, localize, and concentrate elements is gained by investigating biologically controlled biomineralization processes. Such studies yield information on how minerals are nucleated, spatially segregated, their internal microstructure and bulk shape determined and how inorganic/organic interfaces are controlled. The organic matrix is generally assumed to play an important role in crystal growth as well as contributing to the biomechanical properties of the mineralized tissue formed (Weiner, 1984). In many mineralized tissues, the organic matrix forms a two- or three-dimensional structure onto which or into which the crystal grows. The two categories of matrix components have

been called ''framework'' and ''surface'' constituents, for the more hydrophobic–insoluble macromolecules and the more acidic soluble macromolecules, respectively (Weiner et al., 1983). A general mode of biomineralization that addresses several levels of biomineral formation has been suggested by Mann (2001). Good sources of information on these topics are provided by Bäuerlein, 2000; Weiner and Dove, 2003; Wilt et al., 2003; Bouligand, 2004; Bäuerlein et al., 2007 (see also Table 1).

The active role of organic matrix in biomineralization is fundamental because it represents a source of inspiration for future nanotechnologies with a bottom-up approach (Sanchez

Table 1
History of demineralization

Year	Events and discoveries	References
16th century		
1552	''Tooth-worm'' de-worming technique is first described	Boorde (1552)
17th century		
1670	''The Vain Speculation Undeceived by Senses. Response Letter About the Petrified Marine Objects that are Found in Different Inland Locations'' is published	Scilla (1670)
18th century		
1728	Pierre Fauchard writes the ''Le Chirurgien Dentiste''; he rejects the toothworm theory of dental caries and describes enamel hypoplasia as ''an erosion of the enamel''	Cited by Hoffman-Axthelm (1981)
1754	Tooth-worm in ''Onomatologia medica''	Von Haller (1754, 1756)
1757	Images of tooth-worms are published	Schäffer (1757)
1766	Alexander Blackrie develops Blackrie's Lixivium for dissolution of kidney stones	Blackrie (1766)
1771	''The Natural History of Human Teeth'' is published	Hunter (1771, 1778)
1777	First observations of stone deterioration through biological processes	Knight (1986); Liebig (1853)
1784	First description of morphology of the fish (*Anarchichas lupus*) teeth; author considers the dentine as a variety of bone	Andre (1784)
19th century		
1800	The history of teeth is published	Schreger (1800); Lehner and Plenk (1936)
1823	Discovery of chitin in cuticles	Odier (1823)
1826	First description of the sponge-like boring organism within the valves of oysters	Osler (1826)
1829	''Anatomy, Physiology and Disorders of the Teeth'' is published	Bell (1829)
1829	Amphibian dermal scales and osteoderms, description, demineralization and fine structure studies start	Mayer (1829a,b); Cockerell (1912); Zylberberg and Castanet (1980); Zylberberg and Wake (1990)
1840	''Odontography'' including classification of the different types of dentine is published	Baillere (1840)
1845	First description of endolithic boring foraminifera	Quenstedt (1845–1849); Venec-Peyre (1996); Wisshak and Rüggeberg (2006); Bromley et al. (2007)
1845	Review on demineralization of invertebrates skeletons using acids and alkali	Schmidt (1845)
1849	Studies on microscopic structure of the scales and dermal teeth of some fishes	Williamson (1849)
1849	Studies on the ''excavating powers of certain sponges''	Hancock (1849); Nassonov (1883); Leidy (1889)
1850	Microscopic anatomy of human teeth	Czermak (1850)
1852	Decalcification of mollusc shells using hydrochloric, acetic and formic acids	Leydolt and Sitzunsber (1852, 1856); Schmidt (1924, 1928)
1852	''Handbook of Human Tissue Study'' is published	Von Kölliker (1852)
1854	First description of the accessory boring organ of molluscs	Troschel (1854)
1856	Discovery of Sharpey's fibers—as fibers which had perforated into lamellar bone from the surrounding periosteum	Sharpey and Quain (1856)
1857	Discovery of ''halisteresis'' as the possibility of calcium loss by living bone without its obligatory and simultaneous resorption	Kilian (1857)
1859	First evidence of the presence of boring ''unicellular fungi'' (algae) in hard tissues of molluscs, balanids, corals and other animal groups	Von Kölliker (1859a, 1860a,b)
1859	Demineralization of spongin and chitin	Heintz (1859)
1859	''The Physiological Anatomy and Physiology of Man'' is published	Todd and Bowmann (1859)
1859	Microscopic structure of the skeleton of osseous fishes is described	Von Kölliker (1859b)
1863	First report on demineralization of diatoms	Schultze (1863)
1864	Desilicification of Hyalonema glass sponge	Von Kölliker (1864)
1864	Discovery of canaliculi boring by fungus in both recently deposited and fossil bones	Wedl (1864)
1865	Crystal formations in plant cells are described	Rosanoff (1865, 1867)
1866	''Overview of Crystalline Minerals in Table Form'' is published	Bütschli (1866)

Table 1 (*Continued*)

Year	Events and discoveries	References
1872	Fungoid sporangia with filamentous processes are found in shells of molluscs	Stirrup (1872)
1872	Discovery of ''spiculin'', collagen and other organic components after demineralization of calcareous sponge spicules	Haeckel (1872); von Ebner (1887); Sollas (1885); Weinschenck (1905); Travis et al. (1967); Ledger (1974); Aizenberg et al. (1995, 1996); Sethman and Wörheide (2008)
1873	Discovery of osteodentine in the teeth of some of the lower vertebrates	Heincke (1873)
1875	''Treatise on Dental Caries'' is published	Magitot (1875, 1867)
1877	Dissertation on studies of the origin of calcareous minerals in plants is published	Melnikoff (1877)
1877	Discovery of plant cystoliths	De Bary (1877); Molisch (1882); Chareyre (1885)
1878	Thermochemical studies on water-containing salts	Thomsen (1878)
1878	''On the Caries of the Teeth'' is published	Leber and Rottenstein (1878)
1880	''On the Action of a Lichen on a Limestone'' is published	Sollas (1880)
1881	Willoughby D. Miller finds that acid produced by microorganisms causes caries of the enamel	Miller (1883)
1881	Studies on the skeleton of radiolaria	Bütschli (1881)
1882	Discovery of vasodentine in the teeth of pike (*Esox lucius*)	Sternfeld (1882)
1883	Chemical theory of hard substrates' dissolution by boring sponges first established	Nassonov (1883); Cotte (1902); Warburton (1958); Cobb (1969)
1885	First observation of ''an inner gelatinous uncalcified nucleus'' after the decalcification of ascidian spicules	Sluiter (1885)
1886	Dental caries is recognized as a process that may show ''decalcification''	Magitot (1886)
1887	Histology of the teeth	Weil (1887)
1887	*Mycelytes ossifragus*—fungus producing bored channels in bone	Roux (1887)
1888	Desilicification of glass sponge skeletons using HF and KOH	Sollas (1888)
1889	Evidence of the presence of fungi-mediated bored channels in bone and teeth	Schaffer (1889, 1890, 1894)
1889	Discovery of ''hyalodentine''—an osseous layer on elasmoid fish scales	Hofer (1889); Meunier (1984)
1890	Chemo-parasitic theory of the etiology of dental caries	Miller (1890)
1890	First evidence of the presence of carbonate-boring lichens	Zahlbruckner (1890)
1890	First suggestion about the role of chemolithotrofic microorganisms in stone deterioration	Müntz (1890)
1890	Discovery of cellulose, pectin and ''callose'' in plant cystoliths	Mangin (1890a,b)
1890	Morphology of the fish scales including history of hardtissue is described	Klaatsch (1890a,b); Nickerson (1893)
1891	First suggestion that accessory boring organ secretes an acid, chemical theory of the boring mechanism by molluscs	Schiemenz (1891); Turner (1953)
1891	Endolithic fungi in shells are recognized and described	Bornet (1891); Bornet and Flahaut (1889)
1892	Histological studies on coelencerates	Schneider (1892a,b)
1892	''Botanische Mikrotechnik'' (botanical microtechnique) is published	Zimmermann (1892)
1897	Pathology of enamel	Williams (1897); Black (1897)
1898	Winterberg shows that rabbits fed on oats can protect themselves against ingested mineral acids by coupling these with ammonia	Winterberg (1898)
1899	Introduction of decalcified bone as a bone grafting material	Senn (1899)
1899	Susceptibility and immunity in dental caries	Black (1899)
20th century		
1900	Studies on microstructure of artificial and natural silica (tabaschir, hydrophane, opal)	Bütschli (1900)
1901	Dissociation of calcium citrate	Sabbatani (1901)
1901	Isolation of osseomucoid from ox bone	Hawk and Gies (1901)
1902	Boring algae and disintegration of corals	Duerden (1902)
1903	Review on demineralization of skeletons of lower invertebrates	Von Fuerth (1903)
1906	Analysis of dentin and enamel of human teeth	Hinkins (1906)
1906	Demineralization of Acantharia skeletons	Bütschli (1906a)
1906	Studies on influence of KOH on spicules of calcareous sponges	Bütschli (1906b)
1907	Studies on nature of the crystals isolated from crustaceans test and blood	Bütschli (1907)
1908	The solvent action of soil bacteria upon the insoluble phosphates of raw bone meal and natural rock phosphates	Sackett et al. (1908)
1908	Reptilian osteoderms, description, demineralization and fine structure	Otto (1908); Schmidt (1912); Zylberberg and Castanet (1985)
1908	Demineralization of the fish otoliths and isolation of gelatinous organic matrix	Immermann (1908); Maier (1908); Lissner (1925)
1909	''A History of Dentistry'' is published	Prinz (1909)
1911	Bacterial-chemical study of dental caries	Lothrop (1911)

Table 1 (*Continued*)

Year	Events and discoveries	References
1911	Fish scales, demineralization and fine structure, fish scale collagen	Cockerell (1911); Waterman (1970); Onozato and Watabe (1979); Schonborner et al. (1981); Zylberberg and Meunier (1981); Zylberberg et al. (1988)
1914	High ingestion of acid-forming foods appeared to cause decalcification	Steenbock et al. (1914)
1914	The role of phosphoric esterase in decalcification	Bergeim (1914)
1915	Kalklösende Algae	Bachmann (1915)
1920	The origin, growth and fate of osteoclasts and their relation to bone resorption	Arey (1920)
1921	Diaphanol (ClO_2 in acetic acid) as demineralizing agent for animal hard tissues	Schulze (1921)
1921	Development of decalcification solutions containing organic solvents	Jenkins (1921); Scott and Kyffin (1978)
1922	Use of hematoporphyrin for identification of decalcification in bone	McCollum et al. (1922)
1922	Demineralization of marine invertebrates	Clarke and Wheeler (1922)
1922	Coral sclerites as biocrystals	Schmidt (1922a,b)
1922	Study on endolithic limestone lichens	Fry (1922)
1923	Review on microchemistry of animal skeleton substances is published	Schulze and Kunike (1923)
1923	Demineralization of plant encrustations	Schmidt et al. (1923)
1924	Enamel and parasitic processes	Faber (1924, 1928)
1924	Lichenes mediate biodeterioration of historical glass	Mellor (1924)
1925	Review on demineralization properties of cellulose, chitin, conchin, spongin and cornein	Kunike (1925)
1925	Classis ''osteoclasis'' hypothesis is proposed	Pommer (1925)
1926	First studies on morphology of scleral ossicles (bony plates within vertebrates' eyes)	Yano (1926); Edinger (1929); Lemmrich (1931); Franz-Odendaal and Hall (2006); Franz-Odendaal and Vickaryous (2006)
1926	Study on pathological chemistry of the teeth	Toverud (1926)
1927	Bacteria as agents of chemical denudation	Thiel (1927)
1928	''The Normal and Pathological Physiology of Bone'' is published	Leriche and Policard (1928)
1929	Use of magnesium citrate for decalcification of bone	Kramer and Shipley (1929)
1930	Use of X-rays for determining when the decalcification is complete	Hagens (1930)
1930	Microscopical observation of disorganized bone fibrils after decalcification	Bodansky et al. (1930)
1930	''The Resorption of Bone'' is published	Jaffe (1930)
1931	X-ray and histological evidence of decalcification of bones	Shelling (1931)
1932	Decalcifying action of ammonium chloride could be reduced by administration of calcium salts	Jaffe et al. (1932)
1932	Studies on the cause and nature of dental caries	Enright et al. (1932)
1932	Comparative study of histological preparations of bone with different decalcifying fluids	Gooding and Stewart (1932)
1932	The participation of the carbonates of bone in the neutralization of ingested acid: bone demineralization occurs in response to chronic acidosis	Irving and Chute (1932); Bettice (1984)
1933	Decalcification of rats' teeth using 3% HNO_3 in 80% alcohol	Templin and Steenbock (1933)
1933	The relationship of microorganisms to decay of stone	Paine et al. (1933)
1933	The role of the parathyroid glands in deseasis associated with demineralization of the human skeleton is discussed	Compere (1933)
1933	Dissolution of silica-containing plant cystoliths is described	Freiserleben (1933)
1934	Demineralization of bone using 3% KOH in glycerol	Crowell et al. (1934)
1935	Inorganic calcium and phosphate of blood appear to be in equilibrium with the bone salts	Schmidt and Greenberg (1935)
1935	Ancient biosignatures	Abel (1935)
1936	First review on boring (endolithic) algae is published	Fremy (1936)
1936	Studies on bone tumors and osteolytic sarcomas started	Geschickter and Copeland (1936); McInnes and McCullough (1953); Lesure (1958); Guise (2000); Goltzman (2001)
1937	First postulation of the presence of ''*calcase*''—enzyme secreted by accessory boring organ and responsible for demineralization of mollusc shells	Ankel (1937, 1938)
1937	Osteoporotic rat bone is produced by a diet containing calcium carbonate	Harrison (1937)
1937	Calcium carbonate-dissolving algae	Von Pia (1937)
1937	Chemical constitution of enamel and dentine	Armstrong and Brekhus (1937)
1938	''The Dissociation of Some Calcium Salts'' is published	Greenwald (1938)
1938	Decalcification of crustaceans' cuticles using 30% aqueous solution of sodium hexamethaphosphate	Wilks (1938)
1939	Lactic acid associated with the caries process	Miller and Muntz (1939)
1940	Preparation of the enamel organic matrix	Diamond and Weinmann (1940)

Table 1 (*Continued*)

Year	Events and discoveries	References
1940	Plant cystolith skeletons are described and reviewed	Wieler (1940)
1940	Histology and regeneration of the fish scale are described	Neave (1940)
1941	Discovery of accessory boring organ by Muricidae and suggestion of chemo-mechanical theory of penetration	Fretter (1941); Carriker (1943)
1943	Chemolysis of renal calculi by direct irrigation	Suby and Albright (1943); Keyser et al. (1947); Dretler and Pfister (1983)
1944	"The Chemistry of Bone Formation" is published	Kuyper (1944)
1945	Formic acid-sodium citrate decalcification of teeth and bones	Morse (1945)
1945	The pH of the carious lesion	Stephan (1945)
1945	X-ray study on mineral formations of plant, animal and human origin	Brandenberger (1945)
1948	"An Improved Method of Decalcification" using formic acid is published	Kristensen (1948)
1948	First evidence that microorganisms in rhizosphere can dissolve sparingly soluble inorganic phosphate	Gerretsen (1948)
1949	Decalcification of the mother-of-pearl (nacre), isolation of organic components and discovery of stratified membranes of conchiolin	Grogoire et al. (1949, 1950, 1954, 1955); Gregoire (1957, 1959)
1949	Demineralization of enamel and isolation of eukeratin	Block et al. (1949)
1950	Demineralization and classification of diseases in bones	Haldeman (1950)
1950	Bacterial chemistry of dental plaques	Stralfors (1950)
1951	EDTA (Versene) as organic chelating agent for demineralization of hard tissues	Nikiforuk (1951); Sreebny and Nikiforuk (1951); Nikiforuk and Sreebny (1953)
1951	Collagen fibers of bony tissue in the electron microscope	Huber and Roullier (1951)
1952	Acid-mediated demineralization of dental tissues for electron microscopy	Albright et al. (1952); Scott (1952)
1952	EDTA-mediated demineralization of bone for electron microscopy	Robinson and Watson (1952)
1953	Isolation of collagen from mammalian bone using dilute HCl	Eastoe and Eastoe (1953)
1954	First report about the presence of amino acids in fossil bones and shells up to approximately 350 M years old	Abelson (1954)
1954	Control of endpoint of decalcification by fluoroscopy	Waerhaug (1954)
1954	The organic content of chalky enamel is described	Stack (1954)
1954	Preparation of the Inorganic Matrix of Bone is described	Williams and Irvine (1954)
1955	Demineralization against atherosclerosis; Chelation Therapy	Clarke et al. (1955); Ernst (2000)
1955	Electron microscopy studies on normal and caries teeth	Helmcke (1955)
1955	"Bone" is published	McLean and Urist (1955)
1956	Discovery and study on organic matrix of urinary concretions	Boyce and Sulkin (1956); Boyce and Garvey (1956); King and Boyce (1957); Boyce et al. (1958); Boyce (1968)
1956	The basic factors of bone demineralization are published	Morris and Benton (1956); Benton and Morris (1956)
1956	Decalcification of serpulid worms' tubes	Hedley (1956); Bernhardt et al. (1985)
1956	A comparative histological study of fossil and recent bone tissue is published	Enlow and Brown (1956)
1956	"General Anatomy and Histology of Bone" is published	Bourne (1956)
1957	"A Histochemical Study of the Organic Matrix of Hen Egg-shells" is published	Simkiss and Tyler (1957)
1957	Fluoridization of calcium carbonate microfossils	Upshaw et al. (1957)
1958	A quantitative study of decalcification methods	Vardenius and Alma (1958)
1958	"The Chemical Dynamics of Bone Mineral" is published	Neuman and Neuman (1958)
1958	Study on nature and chemical analysis of ossicles—holothurian calcium carbonate-containing sclerites	Hampton (1958)
1958	First evidence of the presence of collagen in human cementum as shown by electron microscopy	Tonge and Boult (1958)
1959	Osteolytic bone is dissolved by aminopeptidase secreted by osteocytes	Lipp (1959)
1960	"Specificity of the Molecular Structure of Organic Matrices in Mineralization" is published	Glimcher (1960)
1960	"Histopatological Technic and Practical Histochemistry" is published	Lillie and Fuller (1960)
1960	Rapid complexometric method for the estimation of calcium in bone, dentine and enamel	Weatherell (1960)
1960	Method for studying the breakdown of synthetic and natural silicates by soil bacteria is developed	Webley et al. (1960)
1961	The mechanism of silica dissolution from diatom walls is described	Lewin (1961)
1961	An osteolytic mucor mycosis in a penguin is described	Bigland et al. (1961)
1961	First report on amino acid composition of the organic matrix of decalcified fetal bovine dental enamel	Glimcher et al. (1961)
1961	Report on the regular occurrence of demineralized collagen fibres at the resorbing bone surface	Hancox and Boothroyd (1961)

Table 1 (*Continued*)

Year	Events and discoveries	References
1961	Decalcification of the sections of calcified tissue on the grids with potassium permanganate, uranyl acetate, or phosphotungstic acid for electron microscopy	Dudley and Spiro (1961)
1962	Comparative studies of bone matrix in normal and osteoporotic bone	Little et al. (1962)
1962	Kinetics of acid demineralization are described	Gray (1962); Birkedal-Hansen (1974)
1962	Decalcification of chicken egg shell and isolation of glycosaminoglycans	Baker and Balch (1962); Bronsch and Diamantstein (1965); Heaney and Robinson (1976); Nakano et al. (2001)
1963	Collagen and a cellulose-like substance in fossil dentine and bone	Isaacs et al. (1963); Shackleford and Wyckoff (1964); Wyckoff et al. (1964); Ho (1966); Pawlicki et al. (1966)
1963	"Principles of Bone Remodeling" is published	Enlow (1963)
1963	"Mechanism of Hard Tissue Destruction" is published	Soggnaes (1963)
1963	"Comparative Biology of Calcified Tissue" is published	Moss (1963)
1964	Macromolecular organization of dentine matrix collagen	Veis and Schlueter (1964)
1964	Lipids in demineralized dentine, proteolipids, phospholipids and lipids in demineralized bone and kidney stone matrices	Dirksen and Ikels (1964); Ennever et al. (1977); Nefussi et al. (1992); Khan et al. (1996); Goldberg and Septier (2002)
1965	Intramuscular implantation of demineralized bone matrix elicits new bone formation, discovery of Bone Morphogenetic Protein	Urist (1965); Urist and Nogami (1970); Urist et al. (1979)
1965	Phenomenon of focal calciolysis in exhumed bones is described	Thurner et al. (1965)
1966	"Preparation of Decalcified Sections" is published	Brain (1966)
1966	"Interactions in Electrolyte Solutions" is published	Nancollas (1966)
1966	Kinetics of enamel dissolution	Gray (1966)
1966	Bacteria can penetrate rock	Myers and McCready (1966)
1966	Historadiographic studies on calciolysis as the initial stage of bone resorption	Bohartirchuk (1966)
1967	"Structural and Chemical Organization of Teeth" is published	Miles (1967)
1967	Discovery of the first acidic protein in vertebrate dentin	Veis and Perry (1967)
1967	"Structural and Chemical Organization of Teeth" is published	Miles (1967)
1967	Scanning Electron Microscopy studies of resorbing surfaces of dental hard tissues	Boyde and Lester (1967)
1968	Isolation of proteins from modern and fossil molluscan shells	Bricteux-Gregoir et al. (1968)
1968	Isolation of lipids and phospholipids from mineralized tissues of fish and other animals	Shapiro (1968); Wuthier (1968)
1968	"Dentine and Pulp: Their Structure and Reaction" is published	Symons (1968)
1969	Phosphoprotein phosphatase catalyzes the rapid demineralization of tooth enamel	Kreitzmann et al. (1969, 1970)
1969	Fungi are considered to be agents of carbonate deterioration for the first time	Krumbein (1969)
1969	*Calcibiocavitology*—the science dealing with the hollowing out of spaces in hard calcareous substrata by organisms	Carriker and Smith (1969)
1969	Carbonic anhydrase is responsible for in vivo demineralization of the valves of lamellibranches by molluscs	Chetail and Fournie (1969)
1969	Evidence of the chemical nature of the boring mechanism by Polydora "mud worm" in calcareous substrates	Haigler (1969); Blake and Evans (1973); Zottoli and Carriker (1974)
1970	"Biological Calcification: Cellular and Molecular Aspects" is published	Schraer (1970)
1970	Fungal attack on rock: solubilization mechanisms	Silverman and Munoz (1970)
1970	The demineralization in the bone of the Teleost fish can be produced in three different ways: osteoclastic, osteolytic and halastatic	Lopez (1970)
1971	"The Metals of Life. The Solution Chemistry of Metal Ions in Biological Systems" is published	Williams (1971)
1971	First ultrastructural study on osteodentin in the pike (*Esox lucius*)	Herold (1971)
1972	Organic acids and chemical weathering	Huang and Keller (1972)
1972	"Chemical Zoology" is published	Florkin (1972)
1973	Uronic acid containing soluble intracrystalline polysaccharides isolated from algal coccoliths for the first time	Westbroek et al. (1973)
1973	Studies on morphology and ultrastructure of shark enamel	Reif (1973)
1974	"Handbook of Histopathology and Histochemical Techniques" is published	Culling (1974)
1974	370 MYO devonian boring algae were described	Kobluk and Risk (1974)
1974	Fungal osteoclasia: a model of bone resorption	Marchiafava et al. (1974)
1974	Biodegradation and utilization of silica in nature	Lauwers and Heinen (1974)
1975	Demineralization of bone matrix: observations using the electron microscope	Thorogood and Gray (1975)
1975	"The Study of Trace Fossils" is published	Frey (1975)

Table 1 (*Continued*)

Year	Events and discoveries	References
1975	Mineral-tetracycline reactions and tetracycines as demineralization agents in bone, teeth and hard tissues	Skinner and Nalbandian (1975); Wikesjö et al. (1986); Sterrett et al. (1997)
1975	Decalcification techniques in electron microscopy	Dietrich and Fontaine (1975)
1976	Isolation of 80 million year old mollusc shell proteins	Weiner et al. (1976)
1976	Demineralization in forensic science	Helfman and Bada (1976); Waite et al. (1999)
1976	Oldest (Upper Silurian) organic remains of boring algae are found	Kazmierczak and Golubic (1976)
1976	SEM study on dentin: demineralization results in shrinkage of the dentin structure	Garberoglio and Brännström (1976)
1976	"Forensic Dentistry" is published	Sopher (1976)
1977	Decalcified bone as a substrate for osteogenesis	Nade and Burwell (1977)
1977	Caries and the remineralization phenomena	Silverstone (1977)
1977	Phosphatic shell formation in brachiopod molluscs and isolation of their shell proteins	Jope (1977); Watabe and Pan (1984)
1977	EDTA demineralization of calcium oxalate stones and discovery of a soluble gamma-carboxyglutamic acid-containing protein in renal calculi	Lian et al. (1977); Warpehoski et al. (1981)
1978	Dissolution of biominerals: a constant composition method	Tomson and Nancollas (1978)
1978	*Anatolepis*—the earliest (520 MYA) presumed vertebrate known to possess a mineralized skeleton is found	Repetski (1978); Smith et al. (1996)
1978	Osteoclast-mediated demineralization and molecular mechanisms of bone resorption	Heersche (1978); Baron (1989); Titelbaum (2000); Väänänen et al. (2000); Titelbaum (2007)
1978	Discovery of calcareous deposits in the renal sac of ascidians and isolation of organic matrix from uric-acid-based spherulites	Saffo and Lowenstam (1978); Lambert et al. (1998)
1978	Direct resorption of bone by cancer cells in vitro	Eilon and Mundy (1978)
1978	Electron microscopy studies on demineralized osteodentine	Kerebel et al. (1978)
1979	Creation of Mutvei's solution as an ideal agent for the dissolution of biogenic carbonates	Mutvei (1979); Schöne et al. (2005)
1979	Discovery of aspartic acid-rich proteins in the soluble organic matrix of mollusc shell	Weiner (1979)
1979	"The Chemistry of Silica—Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry" is published	Iler (1979)
1979	Demineralization of pancreatic stone and isolation of an acidic-rich phosphoglycoprotein	De Caro et al. (1979); Lohse et al. (1981); Multinger et al. (1983)
1979	Etching cells of boring sponges can effect chemical dissolution of calcium carbonate substrates by enzymic digestion via the lysosomal system and membranes of etching cell processes	Pomponi (1979)
1980	"Skeletal Growth of Aquatic Organisms" is published	Rhoads and Lutz (1980)
1980	"Biogeochemistry of Amino Acids" is published	Hare et al. (1980)
1980	Demineralization of ganoid fish scales and isolation of *ganoine*—a superficial hypermineralized layer that lacks collagenous fibers and is true enamel whose organic matrix contains amelogenin	Meunier (1980); Sire et al. (1987); Daget et al. (2001)
1980	"Theory and Practice of Histotechnology" is published	Sheenan and Hrapchak (1980)
1980	The implication of carbonic anhydrase in the physiological mechanism of penetration of carbonate substrata by the marine burrowing sponge	Hatch (1980)
1980	Cytological mechanisms of calcium carbonate excavation by boring sponges are described	Pomponi (1980)
1981	Desilicification techniques are discussed in "Silicon and Siliceous Structures in Biological Systems"	Simpson and Volcani (1981)
1981	"Biological Mineralization" is published	Nancollas (1981)
1981	Symbiotic zooxanthellae enhance boring activity of host sponges	Vacelet (1981); Hill (1996)
1982	"Biological Mineralization and Demineralization" is published	Nancollas (1982)
1982	Antharctic cryptoendolithic microorganisms are described	Friedmann (1982)
1982	Precambrian endoliths discovered	Campbell (1982)
1982	Demineralization of fish otoliths: chemistry, composition, microstructure, organic matrix proteins (OMP-1, Oltolin, zOtolin, otopetrin)	Watabe et al. (1982); Campana and Neilson (1985); Campana (1999); Murayama (2002); Dauphin and Dufour (2003); Hughes (2004); Murayama et al. (2005)
1982	Demineralization of fish scales and isolation of *isopedine*—a tissue consisting of collagen fibrils organized into an orthogonal plywood-like structure	Meunier and Castanet (1982); Meunier (1987)
1983	"Biomineralization and Biological Metal Accumulation" is published	Westbroek and de Jong (1983)
1983	Demineralization of biomaterials: biodegradation that takes place by solution-driven and cell-mediated processes	Klein and de Groot (1983); Nagai and Takeshita (1984); Freyssinet et al. (1993); Koerten and van der Meulen (1999); Lu et al. (2002); Xia and Triffitt (2006)

Table 1 (*Continued*)

Year	Events and discoveries	References
1983	Electron microscopy studies on fossil proteins in vertebrate calcified tissues	Armstrong et al. (1983)
1984	"Calcium and its Role in Biology" is published	Sigel (1984)
1984	Development of demineralization tests and methods for determining the cariogenic potential of foods	Brudevold et al. (1984); Imfeld (1994)
1984	Rapid nitric acid decalcification method	Mawhinney et al. (1984)
1984	"Methods of Calcified Tissue Preparation" is published	Dickson (1984)
1985	Chemical activity of lichens on mineral surfaces	Jones and Wilson (1985)
1985	Rate of dissolution of carbonate sediments by microboring organisms is calculated	Tudhope and Risk (1985)
1986	"Factors Relating to Demineralization and Remineralization of the Teeth" is published	Leach (1986)
1986	Demineralization–remineralization phenomena and human dental decay	Loesche (1986)
1986	Studies on organic matrix of the skeletal spicules of sea urchins and other echinodermates	Benson et al. (1983, 1986); Berman et al. (1990); Kilian and Wilt (1996); Ameye et al. (1998); Wilt (1999, 2002); Seto et al. (2004); Bottjer et al. (2006)
1986	Demineralization of coccoliths and isolation of polysaccharides	Kok et al. (1986)
1986	The microstructure of dentine in taxonomic and phylogenetic studies	Hildebolt et al. (1986)
1987	The oldest microboring cyanobacteria are found in 1500 MYO rocks	Zhang and Golubic (1987); Golubic et al. (2005)
1987	Biogenic etching in amorphous and crystalline silicates	Callot et al. (1987)
1987	"Biodeterioration of Constructional Materials" is published	Morton (1987)
1987	Isolation of intricately patterned organic matrix from ascidian spicules and investigation of factors involved in the formation of amorphous calcium carbonate	Lambert and Lambert (1987); Lambert (1992); Aizenberg et al. (2002)
1987	Coupled diffusion as a basis for subsurface demineralization in dental caries	Anderson and Elliott (1987, 1992, 2003); Anderson et al. (2004)
1987	Demineralization of human calcium oxalate renal stones and isolation of nephrocalcin glycoprotein	Nakagawa et al. (1987)
1988	Review on dental anthropology is published	Scott and Turner (1988)
1988	"The Testimony of Teeth: Forensic Aspects of Human Dentition" is published	Rogers (1988)
1989	"Origin, Evolution and Modern Aspects of Biomineralization in Plants and Animals", "On Biomineralization", "Biomineralization: Cell Biology and Mineral Deposition", " Biomineralization: Chemical and Biochemical Perspectives" and "Skeletal Biomineralization: Patterns, Processes and Evolutionary Trends" are published	Crick (1989); Lowenstam and Weiner (1989); Simkiss and Wilbur (1989); Mann et al. (1989); Carter (1990)
1989	Demineralization of cholesterol gallstones and isolation of 30 kDa acidic protein which regulates the precipitation and accretion of calcium salts	Shimizu et al. (1989)
1989	Osteoclastic bone resorption by a polarized vacuolar proton pump	Blair et al. (1989)
1990	"Ultrastructure of Skeletal Tissues" is published	Bonucci and Motto (1990)
1991	"Calcium Phosphates in Oral Biology and Medicine" is published	Le Geros (1991)
1991	Bioerosion of coral reef—chemical approach	Lazar and Loya (1991)
1991	Biologically mediated corrosion of synthetic glass	Krumbein and Urzi (1991)
1991	"Mechanisms and Phylogeny of Mineralization in Biological Systems" is published	Suga and Nakahara (1991)
1991	Perfusion of demineralization agents by the blood vessels could help to shorten the decalcification process	Nilsson et al. (1991)
1991	Studies on calcium oxalate monohydrate renal uroliths and kinetics of their dissolution	March et al. (1991); Grases et al. (1995)
1992	Isolation of cement precursor and cement proteins from the concrete tubes of sandcastle worms	Waite et al. (1992); Zhao et al. (2005); Sun et al. (2007)
1993	Acidolysis, complexolysis, redoxolysis and mycelial metal accumulation as main mechanisms of fungal-mediated mineral dissolution	Burgstaller and Schinner (1993); Budford et al. (2003); Gadd (2007)
1993	Black fungal colonies induce decay phenomena of antique marbles	Krumbein and Urci (1993)
1993	Discovery of DMP1—novel dentin matrix acidic phosphoprotein	George et al. (1993); He et al. (2003)
1993	Decalcification of otoconia and isolation of organic matrix proteins (otoconin-22, 90, calbindin D28K)	Pote et al. (1993); Davis et al. (1995); Wang et al. (1998); Verpy et al. (1999); Merchan-Perez et al. (1999); Thalman et al. (2001); Thalmann et al. (2006); Piscopo et al. (2004); Huss and Dickman (2003)
1993	Discovery of *hyaloine*—highly mineralized tissue of the fish bony scutes composed of thin vertical fibrils	Sire (1993); Sire and Akimenko (2004)
1993	AFM appeared to offer a powerful new tool to directly evaluate demineralization treatments for dentin	Marshall et al. (1993)

Table 1 (*Continued*)

Year	Events and discoveries	References
1993	The review on dentinogenesis is published	Linde and Goldberg (1993)
1994	Demineralization of diatoms' cell walls and isolation of frustulins (glycoproteins)	Kröger et al. (1994, 1996, 1997)
1994	EDTA- and EGTA-based method for gentle decalcification of the algal cell walls	Morse et al. (1994)
1994	Selective extractability of non-collagenous proteins from chicken bone is described	Gerstenfeld et al. (1994)
1995	"Handbook of Metal–Ligand Interactions in Biological Fluids: Bioorganic Chemistry" is published	Berthon (1995)
1995	Discovery of quartz dissolution by sponges	Bavestrello et al. (1995)
1995	Demineralization of calcium oxalate crystals in plants and isolation of organic matrix	Webb et al. (1995); Bouropoulos et al. (2001); Li et al. (2003); Nakata (2003)
1996	Mechanisms of microbially mediated mineral dissolution	Ehrlich (1996)
1996	"Theory and Practice of Histological Techniques" is published	Bancroft and Stevens (1996)
1996	Bacterial osteolytic factors and mechanism of bacterially induced bone destruction	Nair et al. (1996)
1996	Biotechnological approach for chitin demineralization from shellfish waste by lactic acid fermentation	Zakaria et al. (1996, 1998, 2005); Jung et al. (2005)
1996	First evidence that protein-containing material is trapped within biologically precipitated silica in plants	Harrison (1996); Perry and Keeling-Tucker (2003)
1996	Mineralized tissue is shown to be important in buffering lactic acid during anoxic submergence in reptiles and amphibians	Jackson et al. (1996, 2000, 2003, 2007); Warren and Jackson (2005); Davis and Jackson (2007)
1996	Demineralization of enamel: gastric juice as erosive agent	Bartlett et al. (1996); Bartlett and Coward (2001)
1996	Review on Scanning Electron Microscopy of natural and demineralized bone is published	Boyde and Jones (1996)
1996	An ion exchange method using Dowex ion exchange resin is developed and applied for demineralization of biogenic minerals	Albeck et al. (1996); Gotliv et al. (2003)
1997	Demineralization of molluscs' shells and nacres and isolation of proteins (nacrein, lustrin, perlustrin, pearlin, perlucin, perlwapin, aspein, perlinhibin, perlbikunin, mucoperlin, prismalin, caspartin, calprismin), glycoproteins and acidic polysaccharides	Matsushiro et al. (1997); Shen et al. (1997); Sudo et al. (1997); Matsushiro (1999); Mann et al. (2000); Weiss et al. (2000); Miyashita et al. (2000); Marin et al. (2000); Gotliv et al. (2003); Marxen et al. (2003); Suzuki et al. (2004); Tsukamoto et al. (2004); Marin et al. (2005); Marin and Luquet (2005); Dauphin (2006); Marie et al. (2007)
1997	"Geomicrobiology: Interaction Between Microbes and Minerals" and "Biological Impact on Mineral Dissolution" are published	Banfield and Nealson (1997); Banfield et al. (1999)
1998	Silicates: principles of dissolution	Dietzel (1998, 2000)
1998	Desilicification of demosponge spicules and isolation of silicatein filaments	Shimizu et al. (1998); Cha et al. (1999)
1998	"Decalcification of Bone: Literature Review and Practical Study of Various Decalcifying Agents, Methods, and Their Effects on Bone Histology" is published	Callis and Sterchi (1998)
1998	Organic matrix-mediated remineralization process based on interaction between self-assembled mussel adhesive protein vesicles and apatite	Shirkhanzadeh (1998)
1998	Qualitative and quantitative measurement of enamel demineralization using AFM for the first time	Parker et al. (1998); Finke et al. (2000)
1998	Digestive degradation of a king-sized theropod coprolite is described	Chin et al. (1998)
1998	"Dental Anthropology: Fundamentals, Limits, and Prospects" is published	Alt et al. (1998)
1999	Desilicification of diatoms and isolation of unusual phosphoproteins termed silaffins and long chain polyamines	Kröger et al. (1999, 2002); Poulsen et al. (2003, 2007); Poulsen and Kröger (2004); Sumper and Brunner (2006)
1999	Decalcification of bony samples by EDTA is highly recommended for application in DNA in situ hybridization and comparative genomic hybridization techniques	Alers et al. (1999); Yamamoto-Fukud et al. (2000); Sarsfield et al. (2000); Brown et al. (2002); Gilbert et al. (2005)
1999	Kinetics of enamel demineralization in vitro are described	Margolis et al. (1999)
21st century		
2000	Phenomena of "dark decalcification" in coralline algae and soft corals	Chisholm (2000); Tentori and Allemand (2006)

Table 1 (*Continued*)

Year	Events and discoveries	References
2000	" The Biomineralization of Nano- and Micro-structures" and "Biomineralization: Principles and Concepts in Bioorganic Material Chemistry" are published	Bäuerlein (2000); Mann (2001)
2000	Assessment of decalcifying protocols for detection of specific RNA	Shibata et al. (2000)
2000	Review on phosphate-solubilizing fungi is published	Whitelaw (2000)
2000	Demineralization of bone and calcium regulation during space flight	Doty and Seagrave (2000)
2000	Similarities between the accessory boring organ, osteoclasts, and the mantle of freshwater bivalves suggest that the mechanism for decalcification of calcareous substrates is conserved	Clelland and Saleuddin (2000)
2000	Review: "The Chemistry of Enamel Caries" is published	Robinson et al. (2000)
2001	Crystal dissolution stepwave model	Lasaga and Lüttge (2001)
2001	Method for estimation of the extent of endolithic tissue of the bioeroding sponges	Schönberg (2001)
2001	Biotechnology on the rocks: chrysotile asbestos is converted into amorphous material by chelating action of fungi and lichen metabolites	Fenoglio et al. (2001); Martino et al. (2003); Favero-Longo et al. (2005)
2001	Nanoindentation of dental enamel demineralization and demineralization/remineralization cycles on human tooth enamel surfaces	Finke et al. (2001); Barbour et al. (2003a,b); Lippert et al. (2004a,b); Barbour and Shellis (2007)
2001	"Adhesion-Decalcification Concept" relating to adhesion to and decalcification of hydroxyapatite by carboxylic acids is published	Yoshida et al. (2001); Yoshioka et al. (2002)
2002	"Geomicrobiology" is published	Ehrlich (2002)
2002	Establishing of surface chemistry control on dissolution of all carbonate minerals; possibility to predict the rates from chemical composition of solid and solution	Pokrovsky and Schott (2002)
2003	Nanosized particles: new understanding of demineralization, surface energetic control in dissolution of crystallites and a new model for nanoscale enamel dissolution are described	Tang et al. (2003,2004a); Wang et al. (2005a,b, 2006a)
2003	Mineralization–demineralization cycle in terrestrial isopods and architecture of organic matrix in sternal $CaCO_3$ deposits	Fabritius and Ziegler (2003); Ziegler et al. (2004, 2007); Fabritius et al. (2005)
2003	The demineralization process inactivates infectious retrovirus in infected bone	Swenson and Arnozky (2003)
2003	Silicase, an enzyme which degrades biogenous amorphous silica	Schroeder et al. (2003)
2003	"The Experimental Determination of Solubilities" is published	Tomkins and Hefter (2003)
2003	Discovery of AP7 and AP24—two aragonitic proteins isolated from nacre of the red abalone	Michenfelder et al. (2003)
2003	The use of bacterial oxalate-degrading enzymes to coat urinary biomaterials represents a novel paradigm to reduce biomaterial-related encrustation	Watterson et al. (2003)
2003	Discovery of bacteriomorphic nature of mineral formation in cardiolytes (human heart valves)	Gilinskaya et al. (2003)
2003	"Silicon Biomineralization" is published	Müller (2003)
2003	Review on palaeoecology and evolution of marine hard substrate communities including bioerosion is published	Taylor and Wilson (2003)
2004	HF/HCl demineralization of a 3.5 billion year old Archean chert and isolation of the organic matter	Derenne et al. (2004); Skrzypczak et al. (2004, 2005)
2004	Biologically produced alginic acid affects calcite dissolution and determines microbial deterioration of historic stone	Perry et al. (2004, 2005a); McNamara and Mitchell (2005)
2004	Antarctic cryptoendolitic microorganisms could be suitable models for investigations on extinct or extant life on Mars	Onofri et al. (2004, 2007)
2004	3.5 billion year old biosignatures discovered in Archean pillow lavas	Furnes et al. (2004)
2004	Enamel dissolution and self-preservation of biominerals	Tang et al. (2004b)
2004	The mineralization index as a new approach to the histomorphometric appraisal of osteomalacia	Parfitt et al. (2004)
2004	Use of high-resolution spectroscopic and microscopic techniques to characterize the organo-mineral cell walls of freshwater and marine diatoms	Gelabert et al. (2004)
2005	Demineralization of fossil hard tissues reveals the preservation of original tissues, as well as apparent cells and blood vessels	Schweitzer et al. (2005a,b, 2007); Asara et al. (2007)
2005	Desilicification of glass sponge spicules and the first evidence of the presence of collagen and chitin in their skeletal formations	Ehrlich et al. (2005); Ehrlich et al. (2006); Ehrlich and Worch (2007); Ehrlich et al. (2007)
2005	Microbial interaction with silica and mineralogical footprints of microbial life	Douglas (2005); Perry (2003)
2005	Discovery of *asprich*—a novel aspartic acid-rich protein family from mollusc shell and acidic 8-kDa protein from aragonitic abalone shell nacre	Gotliv et al. (2005); Fu et al. (2005)
2005	Coralline alga: cell wall decalcification as part of epithelial cell replacement	Pueschel et al. (2005)
2005	"Biominerals" is published	Skinner (2005)
2005	EDTA-mediated calcite dissolution demonstrates that, after penetration through a critical pit depth barrier, step velocity increases linearly with the pit depth	Perry et al. (2005b)

Table 1 (*Continued*)

Year	Events and discoveries	References
2005	Mechanism of classical crystal growth theory explain quartz and silicate dissolution behavior	Dove et al. (2005)
2005	Biosilicified structure–function relationship is described	Wang et al. (2005a)
2006	Plausible mechanism for the bioboring on carbonates proposed	Garcia-Pichel (2006)
2006	Boring sponges: establishment of method for measurement of the rate of chemical bioerosion	Zundelevich et al. (2006)
2006	Comparison of six different methods for extracting amino acids and proteins from marine sediments	Nunn and Keil (2006)
2006	Modern review of methodologies for extracting plant-available and amorphous silica from soils and aquatic sediments	Sauer et al. (2006)
2006	Acid-induced demineralization in vitro and dissolution kinetics of primary and permanent tooth enamel	Wang et al. (2006a,b)
2006	Surface chemistry, solubility and dissolution kinetics of plant phytolites is described	Fraysse et al. (2006)
2007	"Biomineralization-Medical aspects of Solubility" is published	Königsberger and Königsberger (2007)
2007	"Function of Eggshell Matrix Proteins", "Biological Calcification: Normal and Pathological Processes in the early Stages" and "Handbook of Biomineralization" are published	Huopalahti et al. (2007); Bonucci (2007); Bäuerlein et al. (2007)
2007	Endolithic microborings on early Earth and applications to astrobiology	McLoughlin et al. (2007)
2007	Osteoclasts have the ability to demineralize calcified elastin	Simpson et al. (2007)
2007	Differentiating human bone from animal bone: a review of histological methods is published	Hiller and Bell (2007)
2007	HCl-mediated demineralization and studies on homology and phylogeny of chondrichthyan tooth enameloid	Gillis and Donoghue (2007)
2008	"Biomineralization: From Nature to Application" will be published	Sigel et al. (2008)

"Everything that a scientist does is a function of what others have done before him; the past is embodied in every conception and even in the possibility of its being conceived at all" (Medawar, 1979).

et al., 2005; Lee and Choi, 2007). The building of discrete or extended organic architectures in biomineralization often involves hierarchical processing in which the molecular-based construction of organic assemblies is used to provide frameworks for the for the synthesis of organized inorganic materials which in turn are exploited as prefabricated units in the production of higher order complex microstructures (Lakes, 1993; Mann, 1995; Aizenberg et al., 2005; Meyers et al., 2006; Fratzl, 2007; Pouget et al., 2007). Animal skeletons have been appear to have been optimized by natural selection to physically support and physiologically maintain diverse tissue types encompassing a variety of functions.

Increased understanding of biomineralization has initiated developments in biomimetic synthesis with the generation of synthetic biomimetic materials fabricated according to biological principles and processes of self-assembly and self-organization (Green et al., 2002). Of course, the materials chemistry aspects of biomineralization can be studied by utilizing model systems, for optimizing the engineering of materials with specialized function. Biocomposites show us novel ways to construct useful materials. We are trying to mimic the natural materials and processes when we design new biomaterials. Therefore, demineralization as a tool is an inevitable step in all modern strategies relating to investigations of biomineralization phenomena and explore the biomimetic potential of naturally occurring materials.

Although the biomineralization phenomena are probably one of the most widely studied topics in modern materials science, biomedicine and biomimetics, a review relating to modern views on the basic information on demineralization and its molecular mechanisms, including kinetic peculiarities, needs our attention as it has been lacking up to now.

3. Demineralization phenomena occurring in nature

Biological mineralization and demineralization play a vital part in our life and the environment around us (Liu and Lim, 2003). And it is the removal of the mineral component that permits access to the organic matrix by extracellular organic compounds produced by biological. The possibility of this kind of attack, and cellular remodeling, that is in many respects functionally similar to the chemical dissolution mechanisms of demineralization.

Thus, demineralization is the process of removing minerals, in the form of mineral ions, from biominerals that takes place both in nature (physiological and pathological demineralization in organisms and bioerosion), and in laboratories, where the dissolution of mineral phases is determined by the practical goals or pure scientific interest relating to the isolation and investigation of organic matrix (Fig. 1). To investigate the controlling mechanisms typically found in bioorganic materials and matrices new techniques can be identified to mimic the regeneration of these "hard" tissues which ensures that the resulting bionanostructure and mechanical properties will be the same as or very similar to those of the natural tissue (Liu and Lim, 2003).

To understand the fundamental processes leading to demineralization, we must first focus on the phenomena that many natural systems have in common. At the very early stages of tissue organization and mineral nucleation are the most general needs, after which specific control of mineral processes including dissolution would allow differentiation into characteristics unique to each organism or organ. For example, in vivo bone remodeling and tooth caries share the same first step—dissolution of the mineral phase by the generation of low

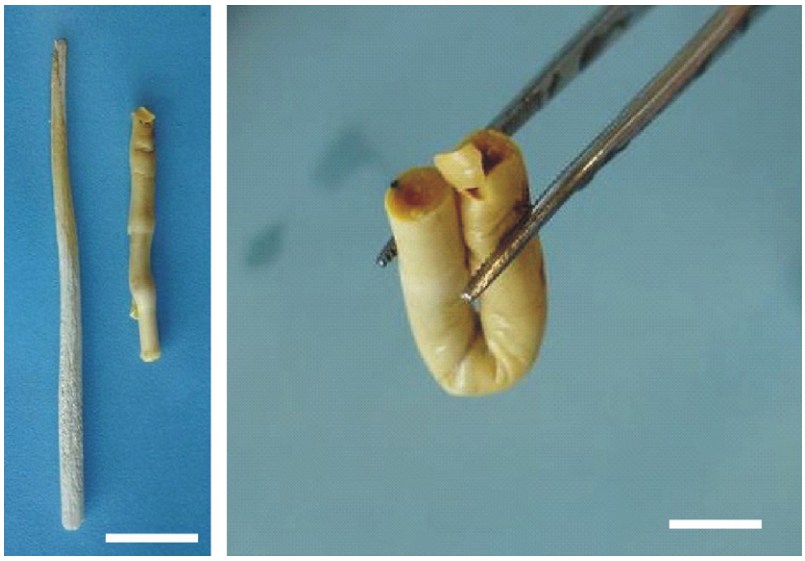

Fig. 1. Demineralization in vitro of the stony hard calcite skeleton of the sea pen coral (Pennatulaceae) in vitro. Demineralization using Osteosoft (EDTA) solution led to loss of mineral phase (left), after that highly flexible organic matrix (right) could be obtained (scale bars = 2 cm and 1 cm, respectively) (image courtesy S. Heinemann).

pH solutions (Collins et al., 2002), however the origin of these processes in these distinct structures are different.

Physiological demineralization has been investigated in human and animal organisms, including invertebrates. Most attention has been focused on bone resorption as a necessary event during bone growth, tooth eruption and fracture healing. These processes are also necessary for the maintenance of an appropriate level of blood calcium (Väänänen et al., 2000). Osteoclasts are the primary bone-resorbing cells in both normal and pathologic states (Roodman, 2001). At normal physiological conditions bone resorption depends on the formation, by osteoclasts, of an acidic extracellular compartment wherein matrix is degraded (Blair et al., 1989). The bone demineralization involves acidification of the isolated extracellular microenvironment, and the process is mediated by a vacuolar enzyme known as H^+-adenosine triphosphatase (H^+-ATPase) in the cell's ruffled membrane (Titelbaum, 2000). The intra-osteoclastic pH is maintained, in the face of abundant proton transport, by an energy-independent $Cl^-/HCO_3{}^{2-}$ exchange on the cell's antiresorptive surface. Finally, electroneutrality is preserved by a ruffled membrane Cl^- channel, charge-coupled to the H^+-ATPase. The result of these ion transporting events is secretion of HCl into the resorptive microenvironment, generating a pH of approximately 4.5 (Silver et al., 1988). This acidic milieu first mobilizes bone mineral in the process of demineralizing the organic component of bone which is subsequently degraded by a lysosomal protease (Titelbaum, 2000).

Osteoclast-mediated demineralization is also described in several pathological states including osteoporosis (Titelbaum, 2000), vascular calcification of aortic elastin (Simpson et al., 2007), renal tubular (Morris and Sebastian, 2002) and metabolic acidosis (Disthabanchong et al., 2002), and different cancer diseases (Roodman, 2001). Tumor cells, in turn, can produce a spectrum of skeletal manifestations which spans diffuse osteopenia, focal osteolysis, focal osteogenesis, and osteomalacia (Goltzman, 2001). In order for tumor cells to grow and invade mineralized bone, osteolysis must occur. Osteoclasts appear uniquely adapted to produce the microenvironment and the biochemical milieu that are needed to resorb bone. Although previous reports have indicated that some tumor cells appear capable of assuming an osteoclast phenotype and directly resorbing bone (Eilon and Mundy, 1978), the bulk of the evidence suggests that most tumor cells act indirectly by co-opting the physiologic mechanisms that normally favor bone resorption. Thus, they release agents such as hormones, eicosanoids, growth factors, and cytokines into the bone microenvironment, which act on osteoblastic stromal cells to enhance the production of osteoclast-activating factors.

Bioerosion is the second important example of demineralization occurring naturally with a history as long as that for biomineralization, It is known to be a major process driving the degradation of carbonate skeletal material and rocky limestone coasts in all marine and some freshwater environments (Wisshak et al., 2005). In concert with biologically mediated demineralization, physicochemical dissolution and mechanical abrasion are rampant is these environments. Thus, most of the research into modern and ancient bioerosion has been conducted on the degradation of calcium carbonate substrates such as corals, shells and limestones, resulting in the production of fine fractions of carbonate sediments (Fig. 2).

If a biomineralized structure are considered as a composite of organic matrix (protein, polysaccharide, lipid) and mineral, then three pathways of demineralization in the natural environment have been identified (Collins et al., 2002):

- chemical deterioration of the organic phase (1);
- chemical deterioration of the mineral phase (2);
- biological (microorganisms, enzymes) attack of the composite (3).

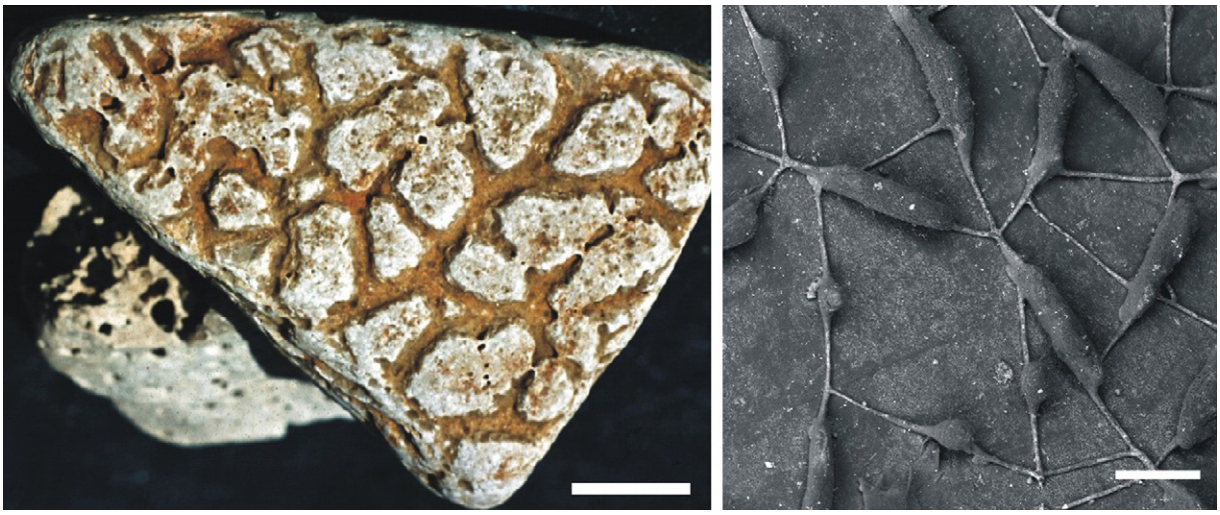

Fig. 2. Bioerosion. (Left) Drilling traces performed by boring sponge *Cliona vermifera* (image courtesy W.E.G. Müller) (magnification: ×0.5). (Right) SEM image shows an artificial cast of the holes (borings) in a bivalve shell made by a Late Jurassic ctenostome bryozoan. Like all bryozoans, this species was colonial, comprising a series of individuals (zooids) produced by asexual budding. The zooids are elongate structures, the thickened parts being where the polypide (gut and tentacles) would have been located when they were alive. Each zooid opened onto the surface of the shell via an orifice at its distal end; orifices cannot be seen as they face into the frame. Narrow stolons link the zooids. The colony was growing predominantly upwards on this image, with the oldest zooids are at the bottom of the frame and the younger at the top (image courtesy P. Taylor) (scale bar = 200 μm).

The first of these three pathways is relatively unusual in that it is extremely difficult to dissolve or alter the organic phase without first or simultaneously effecting the intimately associated mineral phase and will only occur in environments that are geochemically stable for the mineral component. However, because rates of biomolecular deterioration in the burial environment are slow, such biocomposite destruction could yield useful biomolecular information. In most environments, biocomposites are not in thermodynamic equilibrium with the soil solution, and undergo total chemical deterioration.

Dissolution of the mineral exposes the organic matrix to microbially determined deterioration (biodeterioration), and in most cases the initial phase of dissolution will be followed by microbial attachment (pathway 3).

Biological attack also proceeds by initial demineralization; therefore paths 2 and 3 are functionally equivalent. However, in a biocomposite that follows path 3 the damage is more localized than in path 2, and regions equivalent to path 1 may therefore exist outside these zones of destruction (Collins et al., 2002).

Bioerosion is determined by the endolithic mode of life which has a long history. Many microbial endoliths can tolerate extreme environmental stresses, including repeat desiccation, intense ultraviolet irradiation, oligotrophy, and temperature extremes that make them strong candidates for the colonization of early Earth and planetary surfaces (McLoughlin et al., 2007). The oldest microboring organisms found preserved in silica layers have been identified as cyanobacteria. They were discovered penetrating ancient stromatolites in 1500 million year old rocks of the Dahongyu Formation in China (Zhang and Golubic, 1987). Bioerosional organisms are classified (Davis, 1997) into two groups based on their bioerosional activities:

1. Forming and leaving the evidence of their activity as voids which are known for endolithic cyanobacteria, algae, fungi, clionid and other sponges, phoronids and polychaetes, insects and higher plants, the activities of which result in partial or complete replacement of solid substrates with voids.
2. Mechanical abrasion see as rough surfaces on deposits of molluscs, fish bone/or regular echinoids, which mechanically abrade substrates through the action of radulae or teeth fungal hyphae produce fine borings of uniform diameter, which are quite similar to those produced by the filamentous cyanobacteria, but the particular shape of the voids created assists in their identification and classification of their action on corresponding substrate (Golubic et al., 2005). Dichotomously branched and finely tapered openings are commonly observed in endolithic fungi but not in endolithic cyanobacteria and algae. In addition to producing fine exploratory hyphae with possible trophic functions, bag-shaped holes swellings of endolithic fungi are often connected to the substrate surface by wider tunnels, which probably serve for the dispersal of spores. Coral reefs are the most fascinating objects relating to studies on the specificity of bioerosion. The structure and form of the highly complex coral reefs are mainly the result of the interaction between two processes: construction and destruction (Zundelevich et al., 2006). Reef growth is mainly attributed to skeletal deposition by organisms secreting a calcium carbonate skeleton, such as stony corals, molluscs, polychaetes, and crustose coralline algae.

The agents of destruction are biological, physical and chemical, and in many cases their effect on the erosion is synergistic. Physical erosion is caused by wave movement, storms, etc. Chemical erosion involves dissolution of the $CaCO_3$ framework and is mainly mediated or initiated and promulgated by biological activity. Carriker and Smith (1969)

demonstrated experimentally that chemical dissolution is carried out by different penetrants created by the borers: acids, chelating agents and specific enzymes (carbonic anhydrase) as well as non-specific esterases, acid and alkaline phosphatases, decarboxylases, and transaminases (Carriker and Smith, 1969).

Another example of naturally occurring demineralization is the so-called phenomena of dark decalcification (Tentori and Allemand, 2006). Kawaguti and Sakumoto (1948) noted ''intake of Ca^{2+}'' in all scleractinian corals exposed to light and ''output of Ca^{2+}'' in all corals exposed to dark. They argued that the skeleton formation was favored by the alkaline pH (8.84–9.15) of the incubation medium, which was assumed to be result of photosynthesis by zooxanthellae in the coral; correspondingly, the drop in pH (8.00–7.80) in the dark was the reason for the ''resolution of the skeleton [sic]'' (Kawaguti and Sakumoto, 1948). Chisholm (2000) observed dark decalcification in coralline algae incubated at various depths, and explained this as a result of previous light exposure or the acidification caused by cell respiration. It is also possible that the tissue recovery verified visually underwater was overestimated and that decalcification was due to tissue injury. Experiments on soft corals (*Sarcophyton* sp. and *Sinularia* sp.) indicated that these corals also decalcify in the dark (Tentori and Allemand, 2006). These authors suggest that diurnal calcification–decalcification cycles probably control coral sclerite size and shape.

Interestingly, the agents, principles and mechanisms of chemical dissolution that are found or take place in natural environments reported above seem to parallel to explanation of demineralization processes in vitro. Better understanding of the mechanisms leading to demineralization of biominerals in natural environments and better characterization of reaction conditions might allow us to more clearly identify specific characteristics useful for the development of new techniques based on gentle, biologically inspired demineralization.

4. Remineralization

Living forms appear to create specialized environments in concert with the biomineralized tissues formations and probably have been doing so since life first appeared (Skinner, 2005). Biomineralization and demineralization phenomena as described above are only two parts of the mineral–organic matrix circuit occurring in such specialized environments in nature (Fig. 3). The third part of this biochemical cycle is remineralization.

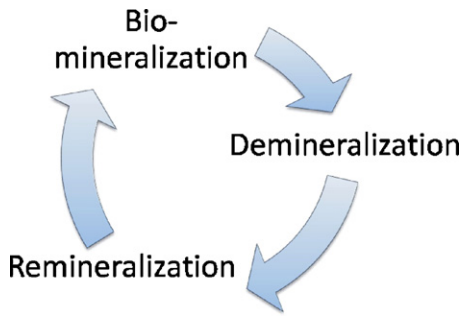

Fig. 3. Schematic view of ''biomineralization–demineralization–remineralization'' cycle occurring in nature.

Remineralization is the process of restoring the solid minerals – though the transfer of anions and cations – to a nucleation sites where the lattices leading to mineral structures are generated. This process follows demineralization and is observed both in vivo in a host of natural environments. A remineralization process in vitro has also been established.

De- and remineralization are critical to the formation of teeth, caries and teeth erosion. Saliva, is a major destabilizer of erupted teeth which may be affected by pH in the oral cavity (Lagerlöf and Olivery, 1994). Both demineralization and remineralization occur on the surface of the tooth and can be considered as dynamic processes, characterized by the flow of calcium and phosphate out of and back into tooth enamel, which should be balanced in order to prevent the progression of caries (Torrado et al., 2004). Demineralization progressing to cavitation occurs if the frequency and magnitude of acid production overwhelm the repair process. This situation would occur in the case of frequent eating or if the repair process is compromised by a reduction in salivary flow (Loesche, 1986). Remineralization dominates if the plaque acid production is restricted, as occurs with the ingestion of low sucrose diets or the use of sugar substitutes for snacks between meals. It involves carbon dioxide from breath and water from saliva to create a mild, unstable carbonic acid that is at the core of the natural remineralization process. Minerals in saliva present from food are dissolved by the carbonic acids. In addition, carbonic acid quickly and easily converts itself to carbon dioxide and water under these conditions (Rantonen and Meurman, 2000). When this happens, the dissolved mineral ions precipitate out as solid mineral ions again, but not always as the original mineral molecules. For example, fluoride also promotes remineralization, and this may be the main mechanism by which fluoride protects in turn tooth decay. When present in the liquid phase during the remineralization of demineralized enamel, fluoride will be incorporated into already existing crystalline mineral and the enamel becomes more resistant to demineralization (Lagerlöf and Olivery, 1994).

Since natural remineralization is frequently inadequate to maintain strong enamel, the natural remineralization process needs to be augmented. When dentine is demineralized by the caries organism, either in an experimental animal or human being, it can be recalcified in vivo by local applications of a preparation of calcium hydroxide (Eidelman et al., 1965). The exogenous calcium ion that is applied to an exposed surface of dentin produces an uptake of endogenous phosphate from the fluids of the body. Crystal formation of apatite follows, and the end result is complete remineralization of the matrix (Bang and Urist, 1967).

Recently, artificial carious lesions in enamel have been developed as a useful analogue for natural lesions when studying de- and remineralization, and many different demineralizing systems have been reported for their preparation (White, 1995; Lynch et al., 2007). The essence of the remineralizing concept might be achieved by simultaneously supplying calcium, phosphate, and fluoride ions to the teeth in order to induce the formation of calcium fluorapatite which remineralizes and

strengthens the tooth (Torrado et al., 2004). Therefore intensive investigations into the remineralization potential of new toothpaste and fluid formulations are still in progress.

The demineralization–remineralization phenomenon, which is an example of acid–base homeostasis mechanism in vivo, occurs in different organisms. In molluscs (*Mercenaria mercenaria*) under normal conditions, the animal becomes anaerobic when the valves close (Crenshaw and Neff, 1969). This period of anaerobiosis is accompanied by an accumulation of succinic acid. This succinic acid is produced by the fixation of CO_2, however some of the CO_2 fixed into succinate originates from the shell carbonate when the shell is dissolved to neutralize succinic acid. When a mollusc closes its valves, the concentrations of calcium, total carbon dioxide, and hydrogen ions increase. The increase in calcium was about three times that of carbon dioxide. Correspondingly, the remineralization mechanism starts when the mollusc opens its valves.

Recently, mineralized tissue has been shown also to be important in buffering lactic acid during anoxic submergence in reptiles, specifically the skeleton and shell in different species of turtles (Jackson, 2000), the skeleton and osteoderms in caimans (Jackson et al., 2003), and the femur of amphibians (Warren and Jackson, 2005). A turtle's shell is the major mineral reservoir of its body: over 99% of the total body calcium, magnesium and phosphate, over 95% of the carbon dioxide, and over 60% of the body's sodium reside in the shell and bone. It was shown (Jackson, 2000) that anoxic turtles accumulate high levels of lactate in their blood.

To avoid fatal acidosis, turtles exploit buffer reserves in their large mineralized shell. The shell acts by releasing calcium and magnesium carbonates and by storing and buffering lactic acid. Together with profound metabolic depression, shell buffering permits survival without oxygen for several months at 3 °C. Also in experiments in vitro with powdered turtle shell, it was shown the shell alkalinized the solution, requiring acid titration for pH-stat control, and the amount of titrated acid required increased as solution pH fell. This is consistent with the hypothesis that shell buffers help to neutralize circulating acids and their release during anoxia is a passive consequence of acid demineralization of the shell and bone. Additionally, one intriguing conservation implication is that if mineralized tissues proved vulnerable to demineralization in an acidic environment, then the tolerance of animals to anoxia or hypoxia and, possibly, their metabolism and performance during anaerobic periods could be compromised (Warren and Jackson, 2005).

Remineralization also plays an important role in natural environments. The following experiments were recently described by Le Cadre et al. (2003). To study the pH effects, cultures with pH values ranging from normal (pH 7.9–8.3) marine were prepared using hydrochloric acid to lower the pH to 7. Foraminifera *Ammonia beccarii* was collected and introduced into these different environment scultures. Under neutral pH (7.0) conditions, pseudopodial activities emission was reduced or stopped. Then the animals external mineralized tissues, ''the test'' became opaque as a result of superficial alteration, which is the first stage of test decalcification. Decalcification progressively extended over the whole test, first destroying the mineralized areas of the last chambers, which contain less tissue, i.e. are thinner. After 15 days, only interlocular walls were preserved, giving the test a star-shaped characteristic of an advanced stage of decalcification. If a specimen was maintained in low pH conditions, the entire test was sometimes entirely destroyed and only the cytoplasm, covered with the inner organic layer, remained. On the other hand, if a specimen with a partially dissolved test was placed in a solution at normal pH, it was able to rebuild its test. Remineralization was somewhat different from the original calcification and was accompanied, in most cases, by morphological abnormalities (e.g. abnormal expansions, irregular chamber sizes, wall with concave form).

These observations show that temporary acidification of the environment, causing partial decalcification of the test, is able to induce morphological abnormalities of foraminiferal tests during recalcification. This acidification may be caused by the anthropogenic impacts on a natural cause. In both cases, deformation of foraminiferal tests yields information on environmental characteristics of the area. Therefore the observations on foraminiferal tests and their use as bioindicators of pollution in coastal environments is now one pf the areas under development in the discussion on climate change (Le Cadre et al., 2003).

Similarly, effects of structural conformations were observed in experiments with octocorals. Isolated spicules of the gorgonian *Leptogorgia virgulata* were decalcified using 0.5 M EDTA solution (pH 7.5) and exposed to an artificial seawater solution to evaluate the ability of the spicules matrix to recalcify (Watabe et al., 1986). Recalcification of the decalcified spicule matrices occurred after 48 h in the artificial seawater solution containing NaCl, $CaCl_2$, KCl, $MgSO_4$, $MgCl_2$, and $NaHCO_3$. Decalcified matrices which retained the configuration of normal spicules assumed a form upon recalcification similar to, but not identical with, undecalcified spicules. Recalcification also occurred in the use of decalcified matrices that did not retain the form of normal spicules. Most of the recalcified matrices showed reduced calcium content when compared with normal spicules. The experiments demonstrated that completely decalcified spicule matrices can initiate recalcification and influence mineral form (Watabe et al., 1986).

Thus, morphological abnormalities observed in different biomineral formations during and after remineralization might be common phenomena, because also in case studies using high-resolution transmission electron microscopy and relating to the growth of apatite crystals in the remineralized enamel, similar effects were obtained. The growth of newly formed crystals and the regrowth of pre-existing enamel crystals occurred extensively in remineralized enamel (Tohda et al., 1990). With advancing growth, the crystals came into contact and fused with each other, forming large crystals with hexagonal outlines. Various kinds of crystalline defects, including edge dislocation, low-angle grain boundary, and lattice shifting, were frequently detected between the fusing crystals. These observations confirm the previous suggestion that processes of de- and remineralization (shell, bone resorption, caries) must be regarded as abnormal biomineralization processes (Krampitz and Graser, 1988).

A better understanding of the biomineralization–demineralization–remineralization mechanisms at the molecular level will result in more effective strategies for the development and establishment of novel methods, tools and approaches for science, engineering and medicine.

5. History of demineralization

To accommodate readers with little or no knowledge of demineralization phenomena, we shall begin with a short overview of the scientific history.

It is well known that each generation of scientists adds details, largely re-explaining the same phenomena in new terminology; only on occasion are completely new concepts introduced (Mandel, 1983). In the case of demineralization, the driving force determining progress in investigations was based on problems of human health. Namely toothache stimulated first of all the origin of the hypothesis and studies on dental caries, a recently well-investigated example of demineralization processes which take place in vivo. Dental caries is a complex disease, the ''cause'' of which has received significant research attention during the 19th and most of the 20th centuries. Mostly via observational investigations, different hypotheses on causes associated with dental caries were put forth. The dominant theory at the beginning, the middle of the 19th century, was the ''worm theory'' (Ismail et al., 2001).

The oldest and most pervasive of all views on dental caries depicts the tooth inhabited by a demon in the form of a worm (Mandel, 1983). Most of our information on the origin of the tooth worm is derived from an Assyrian tablet from the 7th century B.C. that was found about 64 years ago (Weinberger, 1948).

The medical historians of ancient India, Egypt, Japan, and China also make reference to the worm as the cause of toothache. The legend of the worm is also found in the writings of Homer, as well as the great surgeon of the middle ages, Guy de Chauliac (1300–1368 A.D.), who still espoused the belief that worms caused dental decay. The famous Flemish surgeon Jan Yperman (who died about 1330) claimed to have observed that the moving worms caused suppuration in the teeth (Gerabek, 1999).

The belief that a worm developed in a bad tooth, started to pick upon the tooth structure immediately and then died as soon as it came into contact with air can be traced back to Paracelsus (1493–1541) (Gerabek, 1999).

The first full text on dental diseases was published in 1728 when Pierre Fauchard, a French surgeon, wrote ''Le Chirurgien Dentiste''. Fauchard rejected the toothworm theory of dental caries. Instead, he described enamel hypoplasia as ''an erosion of the enamel'' and recommended that hypoplastic areas be smoothed using files (Hoffman-Axthelm, 1981).

Although the toothworm theory is absolutely unacceptable from the modern point of view, here we want to include a small remark regarding the occurrence of worms in a natural environment that really burrow into a variety of calcareous substrata such as soft clays, mud, rock, coral reefs and molluscan shells (Fig. 4). Most of them are boring polychaetous annelids and the mechanisms (physical or chemical) of their burrow expansion are still a matter of controversy (Martin and Britayev, 1998).

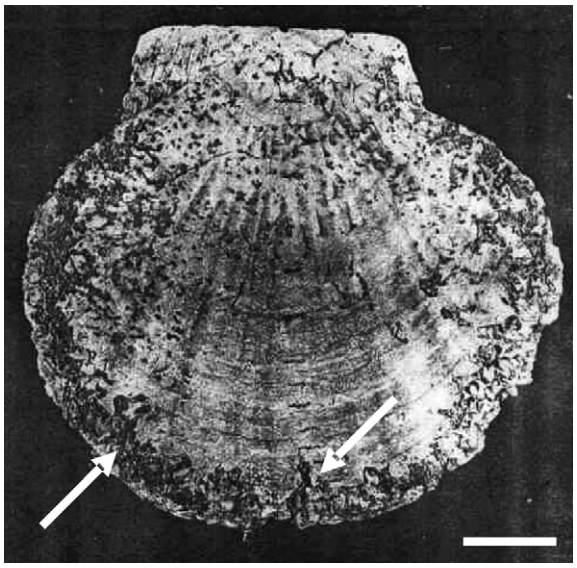

Fig. 4. Boring worms: the outer surface of the scallop *Patinopecten yessoensis* (Jay) shell eroded (arrows) by polychaete worm *Polydora brevipalpa* (scale bar = 1 cm) (image courtesy A.V. Silina).

By 1880, dental caries was defined as a ''disintegration of the tooth substance, molecule by molecule'' (Black, 1880) and a disease that was caused by the fermentation of ''foods'' inside the mouth (MacPhee, 1935). The ''tooth-worm'' theory disappeared as the microscope became more freely available, and investigators began to note the teeming profusion of fungi, and long Leptotrichia-type organisms on the tooth surface and within the carious lesion (Mandel, 1983). In 1880 Weil wrote: ''I regard it quite probable that this fungus *Leptothrix buccalis* bores directly through it (enamel cuticle). The fungi now proceed farther into enamel and force apart its prisms, gradually breaking up its structure'' (Weil, 1887).

Proponents of the chemical theory, such as Tomes (1859) and Magitot (1867), suggested that caries was due to the solvent action of acids generated by the fermentation of food. Dr. W.D. Miller built on the earlier work of Leber and Rottenstein (1878) and fully synthesized two older ideas into a new chemical-parasitic theory of dental decay, generating the data that advanced the speculation of a demonstration that the first step in dental caries was the production of acid by microorganisms fermenting the carbohydrates in the mouth.

Thus, only in 1881, studies by Miller found that acid produced by microorganisms in the mouth caused destruction of the enamel, and caries in dentin resulted from acidic decalcification.

Bacteria were indicted as producing the acids that led to the demineralization of enamel and dentin (Miller, 1883). Once an opening had been made, the microorganisms could then enter into the tooth substance and affect the organic structures (in the dentine?).

Throughout the 20th century, many researches and dentists recognized that dental caries is a product of the interplay of

many factors including local cariogenic bacteria in plaque, fermentable carbohydrates, ''constitutional factors'' related to ''species and strains'', and the tooth structure (Ismail et al., 2001). It took many hundreds of years for the tooth worm to turn and make room for the cariogenic bacteria (Mandel, 1983).

The second topic focusing on demineralization and human health for both scientific and medical interests in 18th century was renal stone diseases. In the early 1760s there was a physician practicing in Bath, Chittick by name, who had a private remedy for urinary calculi, which he kept secret by requiring his patient to supply him with veal broth, to which he added his undisclosed active ingredient (Corner and Goodwin, 1953). Blackrie (1766) a Scottish apothecary at Bromley, Kent, inspired apparently by a combination of altruism and detective curiosity, resolved to identify the drug, which he did by simple chemical tests, as ''a solution of alkaline fixed salts combined with quicklime, or soap lye''. In his work entitled ''Blackrie's Disquisition upon Medicine that Dissolve the Stone'' he gives his method of preparation: ''take eight ounces of pot-ash and four ounces of quicklime fresh from the kiln; mix and put into a glazed earthen vessel; then pour upon them a quart of boiling soft spring-water; let the infusion remain 24 h, stirring it now and then; and afterward filtrate it for use''. It is true that small uric acid and cystine calculi may disappear or decrease in size in alkaline urine, and possibly Blackrie's Lixivium and carbonated water helped in this way if the stone was predominantly of uric acid (Corner and Goodwin, 1953).

Following the revolution in biology and geology in the late 19th century, paleontologists, and some biologists and medical scientists interested in dentition and the skeleton began to study the formation and structure of the ''hard parts'' of an organism. Most of these hard parts were composed of calcium-based minerals, and ''calcification'' became a recognized area of inquiry (Wilt, 2005). Correspondingly development and establishment of different demineralization methods including decalcification (Fig. 5) and desilicification (Fig. 6) techniques with respect to obtain organic matrices continues.

Over the last 50 years, the information on demineralization has grown enormously and this review has attempted to give not only an overview of the history but the current state of knowledge including processes observed and described both in natural environment and in laboratory. See Table 1 for a chronological summary starting in the 16th century. The table integrates events, discoveries, milestone papers and books which elaborate on different aspects of demineralization during the last 400 years.

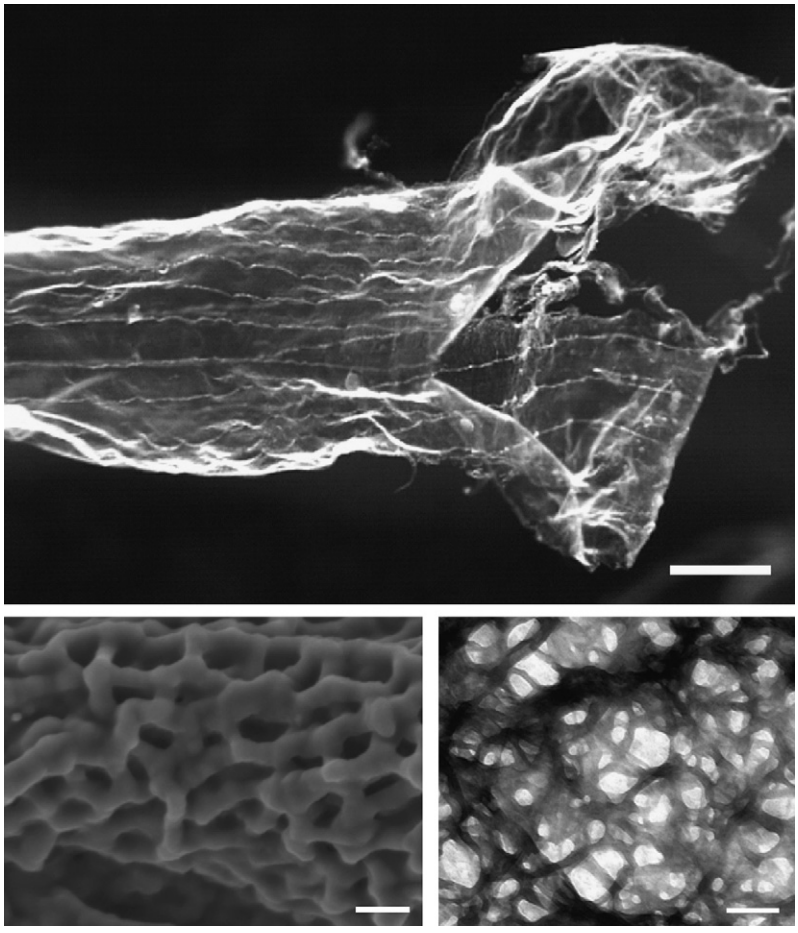

Fig. 5. Demineralization of calcareous skeletons in vitro. Demineralization of bamboo coral nodes (*Isidella* sp.) in Osteosoft (EDTA) solution led to obtaining of the soft organic matrix (above; scale bar = 2 mm). SEM (left, scale bar = 200 nm) and TEM (right, scale bar = 100 nm) images of coral organic matrix show its highly nano-porous structure (images courtesy G. Richter, H. Meissner and P. Simon).

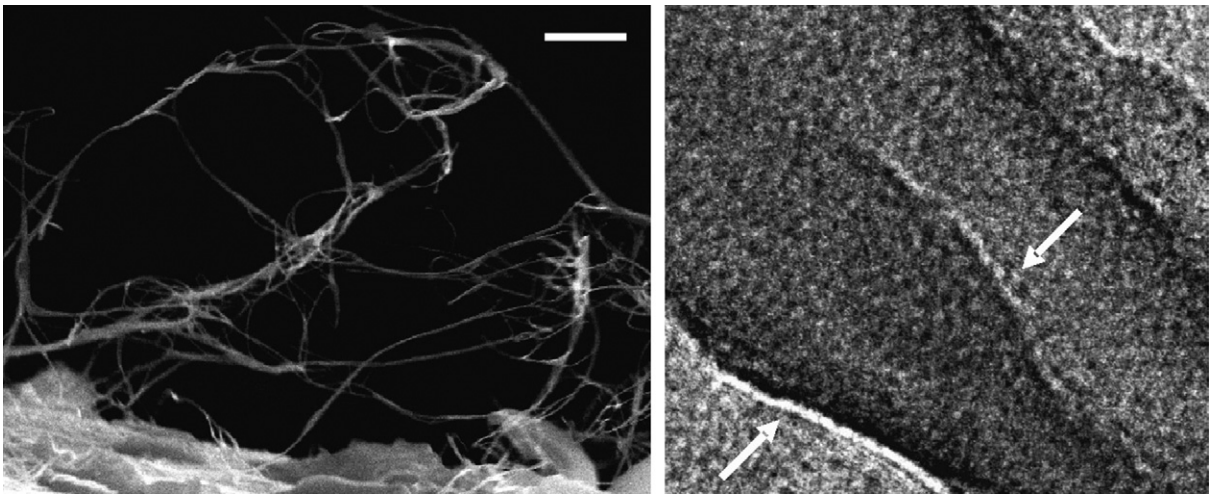

Fig. 6. Desilicification of natural silica-based glass sponge spicules. (Left) SEM image of collagenous fibrillar matrix obtained after alkali treatment of siliceous basal spicules of *Hyalonema sieboldii* glass sponge (scale bar = 1 μm). (Right) High-resolution transmission electron microscopy (HRTEM) image of the fragment of glass sponge collagen microfibril. The arrows indicate the presence of nanofibrillar structures the diameter if which correspond to 1.5 nm (image courtesy P. Simon).

6. Practical applications of demineralization

The data represented in the table shows evidence that scientists from diverging fields, spanning mineralogy, zoology, botany, biochemistry, biogeochemistry, histology, dentistry and materials science, have made great efforts to understand the demineralization mechanism in vivo, in natural environments, and also to mimic the process in vitro using different techniques based on a range of dissolution- and chelation-agents. Additional corroboration regarding the importance of studies on demineralization for the scientific community might be found in the cited papers. More than 10% of articles relating to the problems of demineralization are published in Nature and Science. It must also be cautioned that because of the specificity and vast volume of patent literature relating to demineralization we did not enter information from that information pool for this review.

In conclusion, demineralization is an ongoing, challenging group of mechanisms and aspects applicable and used by different scientific disciplines with their diverse directions including the following:

- evolutionary paleontology (Gould, 1970);
- astrobiology (McLoughlin et al., 2007);
- biomolecular deterioration and survival of organic matter (Collins et al., 2002);
- geomycology (Gadd, 2007);
- paleoclimatology (Schöne and Giere, 2005);
- seawater chemistry (Porter, 2007);
- material chemistry (Dujardin and Mann, 2002);
- geomedicine (Sahai, 2005);
- paleobathymetry (Wisshak and Rüggeberg, 2006);
- exobiology (Onofri et al., 2004);
- osteoarchaeology (Davis, 1997);
- archaeology and bioarcheology (Larsen, 2002);
- histology and histotechnology (Callis and Sterchi, 1998);
- forensic dentistry and forensic science (Rogers, 1988);
- demineralized bone allografts (Herold et al., 2002);
- dental anthropology (Alt et al., 1998);
- mineral dissolution (Nancollas, 1982; Wang et al., 2005b, 2006a,b);
- bio- and chemical weathering (Benzerara et al., 2005);
- medical geology (Skinner and Berger, 2003);
- calcibiocavitology and endolithic microborings (Carriker and Smith, 1969);
- bioerosion (Lazar and Loya, 1991; Garcia-Pichel, 2006);
- remineralization of biomaterials (Liu et al., 2003);
- shell repair and regeneration (Meenakshi et al., 1974; Palmer, 1983);
- sclerochronological studies (Schöne et al., 2005);
- bioremediation (Singh and Ward, 2004);
- bone diseases, osteoporosis, osteopenia, osteoclasia (Skinner, 2000);
- biodeterioration (Morton, 1987);
- taphonomy (Child, 1995);
- archeological bone chemistry (Pate, 1994);
- paleohistory, paleoecology, paleontology (Pate, 1994; Taylor and Wilson, 2003);
- normal and pathological remineralization (Robinson et al., 2000);
- biotechnology (Zakaria et al., 1996, 1998, 2005);
- ageing techniques (demineralization of vertebrae and otoliths) (Correia and Figueiredo, 1997).

We submit here some additional considerations responding to important results which were obtained using demineralization approaches in:

(a) *Modern science*:

Using different demineralization techniques and approaches biologists can precisely reconstruct life-history traits from growth structures (age, growth season, onset of maturity, etc.), and paleoclimatologists and geochemists can identify how much time is contained in each geochemical

sample taken from biogenic hard parts. Accretionary hard parts of many organisms provide excellent archives of past climate and environmental conditions of life history traits. Variable growth rates function as environmental and physiological proxies, and growth increments as calendars. Recognition of growth structures is thus a prime necessity for sclerochronological studies (Schöne et al., 2005).

Microorganisms are agents of decomposition. They grow in and upon rocks and minerals, often relying on their substratum for critical nutrients in order to obtain energy for cell activities. The presence of metabolizing cells on a mineral substrate has a significant effect on the mineral stability and texture and on the geochemistry of the surrounding microenvironment (Douglas, 2005). In addition to inorganic acid production, microorganisms also can catalyze mineral weathering rates by production of organic ligands. Ligands complex with ions on the mineral surface and can weaken metal–oxygen bonds. Alternatively, ligands indirectly affect reactions by forming complexes with ions in solution, thereby decreasing the solution saturation rate. Mineral dissolution rates are important inputs into global climate models (Banfield et al., 1999).

The recovery of biochemical data from bone has a long history (Senn, 1899), which continues to grow as new technical developments enable the recovery of a wider range of biomolecules, including lipids (Stott et al., 1999) and most notably DNA (Donoghue et al., 1998).

To address the important question of the origin of life on Earth, special attention has been paid to the carbonaceous matter in the oldest archean rocks. Finding evidence for traces of early life on Earth is difficult (Brasier et al., 2002; Schopf et al., 2002; Rasmussen, 2000) due to the problems faced in assessing both the syngenicity and the biogenicity of preserved organic matter in Archean sedimentary rocks (Marshall et al., 2006). The discovery of microstructures in cherts (microcrystalline silica) from the Warrawoona Group (Australia), considered as the oldest microfossils on Earth (3.465 billion years old) created a considerable interest in the organic matter contained in this deposit. However, the biogenicity of these microstructures has been recently challenged, which emphasizes the necessity for identifying reliable biomarkers in such ancient organic matter.

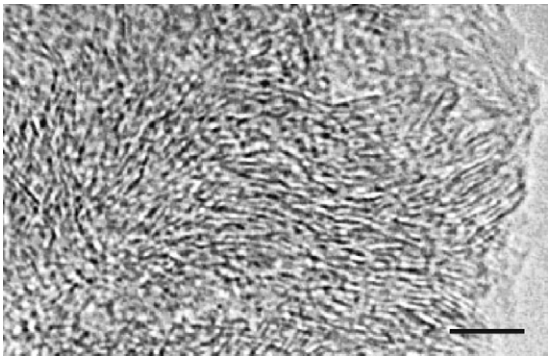

Fig. 7. HRTEM image of organic matter isolated after demineralization of the 3.465 billion years old Warrawoona Chert (image courtesy S. Derenne) (scale bar = 200 nm).

The insoluble organic matter (Fig. 7) was isolated from the bulk sample using the classical demineralization procedure employing HF/HCl. The recovery yield of this acid treatment is 150 ppm of carbon-containing macromolecules. It is in agreement with the low carbon content of the bulk chert. This organic matter has not reached the graphite stage which is encouraging as an indication of early stages of diagenesis not massive alteration of the organic matter. It is similar to a mature kerogen, based on a macromolecular network of large polyaromatic units, but still contains a substantial amount of inorganic cations.

Electron Paramagnetic Resonance (EPR) parameters ascertained the syngenicity of the archean organic matter with terrestrial kerogens. Its chemical structure is consistent with a biological origin and is sharply different from the chemical compositions and structure of the insoluble organic matter of the carbonaceous chondrites.

(b) *Medicine*:

Classic studies by Marshall Urist demonstrated that demineralized fragments of bone could induce bone formation when placed into skeletal muscle, thereby defining the process known as osteoinduction (Urist, 1965; Urist and Nogami, 1970; Urist et al., 1979). The process of demineralization apparently releases bone morphogenetic proteins from the bone matrix, allowing these potent factors to induce stromal cells in the adjacent tissue to differentiate along the osteoblast lineage. Demineralized bone matrix (DBM) preparations lack cells, so they are expected to be most effective when inserted into host sites that contain adequate vascularization and osteoblast precursor cell populations. When placed into a suitable host site in bone organs, DBM can promote new bone formation.

Many different commercially available preparations of DBM have been reviewed by Bauer (2007). They have variable osteoinductive properties, presumably based on differences in processing methods, carriers, and factors related to the donor. Depending on how the bone implant is extracted and processed, different preparations can be composed of granules, strips of interwoven fibers, or puttylike preparations.

7. Epilogue

A significant step forward would be, therefore, to observe, analyze and delineate how Nature performs its complex biomineralization/demineralization/remineralization functions. This ‘‘biomimetic’’ approach may provide necessary information on how inorganic materials form in the biological living environment, not just at the molecular level, but also at the nano/microscale. Further research on the interactions between different biomacromolecules and soluble inorganic species might yield hard, insoluble materials for a variety of purposes.

The three important bioprocesses, biomineralization/demineralization/remineralization, are intimately connected together in an admirable and intriguing fashion in Nature. And it is important to use an integrated approach to study them as a whole some adopting such a research strategy may reveal underlying relationships that, otherwise, may remain unknown.

Understanding how these processes operate in a biological environment can be a valuable guide to developing important industrial processes. Nanoparticle synthesis and engineering is a good example that exemplifies how industrial technologists could learn from Nature (Demadis and Neofotistou, 2007; Knecht and Wright, 2003). No matter the scientific field used to approach these three processes many questions remain. These are the true drivers for multidisciplinary research and such efforts, thus far, have been amply rewarded and have led to great advances. Meaningful progress in our understanding of demineralization depends on continuous developments in areas such as inorganic chemistry, materials science, biology, biochemistry, analytical chemistry, just to mention a few and the development of new tools that will allow for further and deeper understanding of the complex processes occurring in Nature.

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