# **Carbonate minerals**

The most common minerals in this group are the calcium carbonates, calcite and aragonite, while dolomite (a magnesium–calcium carbonate) and siderite (iron carbonate) are also frequently encountered in sedimentary rocks. Calcium carbonate minerals are extremely common in sedimentary rocks, being the main constituents of limestone. Calcite and aragonite are indistinguishable in thin-section: like all sedimentary carbonates, these minerals have a high relief and crystals show two clear cleavage planes present at 758 to each other. Birefringence colours are pale, high-order greens and pinks. The form of calcite in a sedimentary rock varies considerably because much of it has a biogenic origin: the recognition of carbonate components in thin-section is considered in section.

Most dolomite is a diagenetic product, the result of alteration of a limestone that was originally composed of calcium carbonate minerals. When individual crystals can be seen they have a distinctive euhedral rhombic shape, and cleavage planes parallel to the crystal faces may be evident. The euhedral morphology can be a good clue, but identification of dolomite cannot be confirmed without chemical tests on the material. Siderite is very difficult to distinguish from calcite because most of its optical properties are identical. The best clue is often a slight yellow or brownish tinge to the grain, which is a result of alteration of some of the iron to oxides and hydroxides.

## **CARBONATE MATRIX**

### Introduction:

Carbonate mud is the equivalent of clay in terrigenous rocks and can form pure deposits (variously termed micrites, carbonate mudstones, lime mudstones, or calcimudstones on the carbonate side, and claystones or shales on the clastic terrigenous side). Clay-sized particles also act as matrix material that supports larger grains or are lodged interstitially between a self-supporting framework of larger grains. Decades ago, when both life and muds seemed pure and simple, both clays and carbonate muds were viewed as miniature versions of larger grains, acting primarily as reworked particles. It is now known that some clays are detrital, some are altered or neoformed on the seafloor, and some are precipitated during the long diagenetic history that accompanies burial, adding considerable complexity to the interpretation of terrigenous shaly deposits. The same is true on the carbonate side. Carbonate muds can be part of the spectrum of disintegration products of carbonate organisms, some can be formed by direct inorganic precipitation, and some may be formed in association with microbial metabolism. Furthermore, some may be primary sediment that responded to hydrodynamic forces during sediment formation and some may be precipitated interstitially, at or near the seafloor (through organic or inorganic processes), or during later diagenesis. It is even possible for grains to break down into smaller carbonate particles during diagenesis, or for diagenetic conversion of former carbonate mud to a mosaic of coarser calcite crystals (microspar). Although we have learned much over the past decades about mud-sized materials, we are far from having a full understanding of them. We also have not yet developed reliable criteria for the consistent distinction between organically produced and inorganically precipitated materials, or even between detrital particles and authigenic precipitates.

## **Definitions:**

<u>Micrite</u> - An abbreviation of "microcrystalline calcite". The term is used both as a synonym for carbonate mud (or "ooze") and for a rock composed of carbonate mud (calcilutite). Micrite consists of 1 to 4  $\mu$ m-diameter crystals and forms as an inorganic precipitate or through breakdown of coarser carbonate grains. Micrite is produced within the basin of deposition and shows little or no evidence of significant transport (Folk, 1959).

<u>Microspar</u> - Generally 5- to 20- $\mu$ m-sized calcite produced by recrystallization (neomorphism) of micrite; can be as coarse as 30  $\mu$ m (Folk, 1965). Restricted to recrystallization products, not primary precipitates.

**<u>Pseudospar</u>** - A neomorphic (recrystallization) calcite fabric with average crystal size larger than 30-50 μm (Folk, 1965).

## Mineralogy:

Modern marine shelfal carbonate mud is mainly aragonite (with some high-Mg calcite); deep-sea chalk oozes are low-Mg calcite as are most lacustrine calcareous muds. The composition of carbonate muds produced from breakdown of skeletal material are clearly controlled by the mineralogy of those organisms. Paleozoic shells were generally more calcitic than the aragonite-dominated shelled fauna of the modern world. Furthermore, even the mineralogy of "inorganic" marine precipitates (muds as well as cements) is now known to have varied throughout geologic time (Lasemi and Sandberg, 1984, 1993).

### Keys to Petrographic Recognition:

1. Modern carbonate mud consists largely of the breakdown products of organisms (due to decomposition of organic binding materials and abrasion or maceration of shells). Macroscopic algae (especially green algae) are major contributors of needle-shaped, mud-sized, aragonitic particles in tropical platform and platform margin settings. Modern inorganic aragonitic precipitates, in the water column or on the seafloor, also are needle-like (with individual crystals typically 3-5  $\mu$ m in length) and may contribute to carbonate muds.

2. The calcitic micrite of older carbonate rocks was neomorphically formed from mixed mineralogy precursors to form an equant mosaic of 1- to 4- $\mu$ m crystals. The precursor material acted as detrital particles and so may show geopetal fabrics, scattered coarser particles, and other indications of mechanical sedimentation. Inclusions or molds of precursor minerals may be seen within micritic calcites (especially using SEM).

3. Neoformed microcrystalline cement and microbial precipitates may show clotted or peloidal fabrics and can grow in any position within interparticle pores or larger cavities (non-geopetal fabrics).

4. Microspar and pseudospar typically have patchy distributions grading into normal micrite; crystal outlines tend to be elongate (loaf-shaped) or have irregular, sutured boundaries).

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Fig. 5.27 Experimental abrasion of skeletal material. Starting sample (upper left) contained fresh specimens of the bivalve Mytilus sp., the gastropods Aletes sp., Haliotis sp. and Tegula sp., various species of limpets and enchinoids, the starfish Pisaster sp. and the calcareous algae Corallina sp. The series of diagrams shows selective destruction of the assemblage by tumbling (modified after Chave 1964)



Mechanical destruction of skeletal material has characteristic rates of destruction, depending on shell thickness, microstructure and possible prior bio-erosion. A primary factor is the surface area to weight relationship (Fig. 5.27). These differences in abrasion rate may sometimes give rise to a fossil assemblage that deviates markedly from the original composition (Fig. 5.28). In general, in any given abrasive environment, skeletal material with a small surface area per unit weight is generally more durable than those with a large surface area per unit weight.

Biological destruction. As soon as any organism dies, its skeletal material begins a process of deterioration due to the activity of a great variety of organisms. In particular many species of sponges, worms, bivalves, fungi and algae have the ability to sculpt or penetrate hard calcareous substrates e.g. skeletal material lying exposed on the sea bottom. Skeletal material has a low hardness (e.g. low-Mg calcite has a hardness of 3 and aragonite 3.5-4 on Moh's scale of hardness) and is easily dissolved in weak acids which render these substrates attractive for bioeroding organisms. The density and diversity of bioeroding organisms may therefore be high on carbonate material which has been exposed on the sea bottom for a year or more. Bio-erosion is a self-destructive process, and the sculpture that is produced can only be preserved if covered by sediment, which suffocates the endolithic community. Bioerosion increases the vulnerability of skeletal

material to mechanical destruction, with the result that a significant part of carbonate deposits may consist of a combination of bio-eroded and mechanically fragmented material (Fig. 5.29).

# 5.5.8 Micritisation

This process, which was first described by Bathurst (1975), is due to the fact that exposed skeletal fragments within the photic zone may serve as suitable substrates for various green algae, cyanobacteria and fungi. These organisms destroy the surface by boring a fraction of a millimetre into the fragment by secreting acids which dissolve tubular boreholes in which the filaments reside. The diameter of each hole varies somewhat, but usually it is around 5–7  $\mu$ m (maximally 15  $\mu$ m).

When the bioeroding organisms die, each hole gets filled with tiny crystals (micrite) of aragonite or high-Mg calcite. Which crystal type is precipitated depends on the primary mineralogical composition of the shell. Usually the precipitate is aragonite if the shell is aragonite, and likewise for fragments of high-Mg calcite. However, some bacteria can secrete aragonite, and therefore aragonite-fills in empty boreholes may have been produced by bacteria which lived on the algae. In pre-Quaternary sediments low-Mg calcite has usually replaced both high-Mg calcite and aragonite micrites. Repeated borings followed by Fig. 5.28 Examples of breakdown of various skeletal components by mechanical abrasion. Echinoderms, coccoliths and many bryozoans are particularly fragile. (a) Echinoid; (b) ostracod; (c) brachiopod; (d) calcareous red algae; (e) bryozoan; (f) bivalve. Not to scale (modified from Bromley 1980)



precipitation and infilling of the empty cavities cause the fragments to be replaced by a dark micritic coating (Fig. 5.30). The micritised coating is highly stable and is commonly preserved in both Quaternary and pre-Quaternary sediments. Where aragonite fossils have been micritised, the coating (now consisting of low-Mg calcite) often clearly indicates the original shape of the fossil (Fig. 5.31).

# 5.5.9 Microcrystalline Lime Mud (Micrite)

Lime mud deposited in areas with carbonate sedimentation has a grain size of about 1-4 µm. This precludes effective study under an ordinary microscope, only with an electron microscope can each individual grain really be seen.

Carbonate mud (micrite) was previously assumed to be chemically precipitated carbonate, as opposed to fossils or fossil fragments of clearly organic origin. However, a very large amount of modern lime mud, for example from the Bahamas, has been found to consist of aragonite needles from the breakdown of calcareous green algae, particularly *Halimeda*, *Rhipocephalus* and *Penicillus*. This was confirmed partly by studies of the shape of aragonite needles (by electron microscope) and partly through isotope studies of the <sup>18</sup>O/<sup>16</sup>O and <sup>13</sup>C/<sup>12</sup>C ratios in the aragonite mud. The isotope values for the aragonite mud correspond well with the

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Fig. 5.29 Diagram of the dominant size fractions of grains produced by biological destruction of massive corals by endolitic sponges, parrot fish and sea urchins. The endolitic sponges infest calcareous substrates to create a sheltered site for habitation.

Both the parrot fish and sea urchins are important grazers that break down the surface of calcareous substrates in search of epilithic and endolithic plants for food (modified from Scoffin 1987)



Fig. 5.30 Micritisation of a calcareous grain. The process is related to the activities of microboring algae, cyanobacteria and fungi. A micritic envelope is developed if the micritisation is

confined to the outer surface. If the grain is completely micritised, a peloid or cryptocrystalline grain may be the end result. Not to scale (modified from Kobluk 1977)

values one finds for muds formed by various types of algae.

In shallow marine areas near the equator, like the Bahamas, the seawater is often saturated with respect to aragonite. Nevertheless it has not been possible to prove conclusively that any purely chemical precipitation of aragonite takes place in these areas. Sudden whitings of the seawater that are often observed in these areas, has been interpreted as spontaneous crystallisation of aragonite, but the phenomenon can also be interpreted as a disturbance of the lime mud from the bottom, for example by shoals of fish which are present in large numbers where there is whiting of the seawater.



Fig. 5.31 Diagram showing the formation and preservation of a micritic envelope. Skeletal fragments of aragonite may be dissolved and replaced by calcite by one of two processes. *Left*: much of the original structure, such as organic inclusions, may be preserved (albeit not perfectly) through gradual solution of

the skeletal material and immediate precipitation of calcite along a thin solution film. *Right*: complete solution of the skeletal fragment. During later diagenetic stage(s), the mould may be partly or completely cemented by calcite (modified from Bjørlykke 1989)

In areas where strong evaporation and high salinity approach evaporite conditions, such as in the Dead Sea and the Persian Gulf, this kind of chemical precipitation does occur, but only when the salinity is very high, about every fifth year. A sudden proliferation of diatoms could also consume so much CO<sub>2</sub> that the pH rises and causes aragonite to be precipitated.

Microcrystalline lime mud may also be formed by mechanical abrasion. Fossils which lie exposed to wave and current activity will be abraded mechanically, and a fine-grained lime mud formed. However, this process will not produce the well-crystallised aragonite needles of which modern lime muds are found largely to consist. We may therefore conclude that mechanical abrasion of fossils or carbonate fragments is not the main source of lime mud.

Through diagenetic processes, the microcrystalline mud will dissolve and be replaced by microsparite, but this is clearly distinguishable from other sparites, not least by its brownish colour due to incorporated organic matter (Fig. 5.32).

# 5.6 Non-skeletal Grains

Carbonate grains can be classified as skeletal or non-skeletal. Non-skeletal components are defined as grains which do not appear to have been precipitated as skeletal material. However, this neither proves that they could not once have been skeletal, nor that they have an inorganic origin, it only signifies that in their present state no skeletal origin can be ascertained.



Fig. 5.32 The original microcrystalline mud (micrite) has been replaced by microsparite which consists of a mosaic of small brownish crystals. The skeletal remains are dominated by trilobite and ostracod fragments. Thin section seen in plane polarised light. Silurian, Gotland

# 5.6.1 Intraclasts

Intraclasts are erosional fragments of essentially penecontemporaneous carbonate sediment. They are of intrabasinal origin, i.e. were eroded from the sea bottom or adjacent tidal flats and deposited within the area of original deposition. Early cementing, e.g. in the beach zone, or freshwater cementation due to regressions, may result in cemented sediments which are later broken up. We may also find early cementation in a marine environment, forming seafloor hard grounds. If these are then eroded by tidal channels, for example,

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the resulting intraclasts may accumulate as characteristic intraformational conglomerates. Intraclasts can also consist of semi-consolidated pieces of stromatolite.

Intraclasts may be of any size or shape. They are quite common in shallow water limestone facies and are good indicators of early cementation and erosion by currents.

# 5.6.2 Lithoclasts

Lithoclasts, which encompass both intraclasts and extraclasts (or extrabasinal clasts), are produced by the erosion of exposed older or synsedimentary lithified or partially lithified sediment. On carbonate platforms, lithoclasts are normally derived from erosion of the landward margin, where exposed, cemented limestones are broken up by physical, chemical and/or biological processes. Lithoclasts may be of any size or shape, but have generally become well rounded during transport. Because carbonates are vulnerable to weathering and are mechanically weak, the content of extrabasinal carbonate clasts declines with increasing transport distance, particularly in humid climates.

## 5.6.3 Faecal Pellets

Faecal pellets are organic excrements generally produced by mud-eating grazing animals such as crustaceans, worms and molluscs. They are generally round, oval or rod-like in shape and commonly consist of carbonate mud. Most faecal pellets are 0.1–0.6 mm in length and 0.1–0.4 mm in diameter, but can be up to 2 mm long. Animals which eat mud, like snails, bivalves and crustaceans, deposit vast quantities of carbonate mud pellets in carbonate environments, and clay and silt pellets where fine-grained siliciclastic material forms the seafloor. Faecal pellets have a characteristic dark brownish colour imparted by their organic content.

Faecal pellets are produced in all environments, often in well-sorted large quantities forming pelsparite/pelloidal grainstone (Fig. 5.33). Their preservation within a sediment generally requires intragranular lithification, a process occurring in shallow waters which are supersaturated with respect to calcium carbonate. The presence of a low-energy environment is also important to prevent physical destruction. This implies that faecal pellets are most commonly encountered in low-energy, muddy depositional environments in the platform interior.

## 5.6.4 Peloids

The term peloid is used for a polygenetic group of spherical, ellipsoidal or angular grains with diffuse margins but no internal structure. The grains consist of fine-grained carbonate irrespective of size or origin. Because of the diverse origin of the particles, the term peloid is purely descriptive and does not denote origin. Various origins are possible: faecal pellets, micritised grains, intraclasts, a type of abiogenic precipitate, and a microbially mediated precipitate. Most peloids, however, are formed by extensive micritisation of pre-existing carbonate grains which is related to the activities of microboring algae and fungi within the photic zone. Thus, peloids generally indicate shallow, non-agitated waters.

Fig. 5.33 (a) Rounded, rod-shaped pellets. Upper Cretaceous, France. (b) Dark pellets (Pe) in a sandy matrix. Silurian, Oslo Region, Norway. Thin sections as seen in plane polarised light

